COMMISSION OF THE EUROPEAN COMMUNITIES
DG XII – RESEARCH, SCIENCE, EDUCATION

# RAW MATERIALS

## RESEARCH AND DEVELOPMENT

## MATERIALS SUBSTITUTION DOSSIERS

# I. SILVER AND CHROMIUM

June 1980

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# FOREWORD

This series of technico-economic studies on materials substitution has been prepared under the sponsorship of the Commission of the European Communities (Directorate-General for Research, Science and Education). The following most critical commodities have been analysed : Silver, Chromium, Tungsten, Tin.

The decision to carry out these studies stems from concern about the prospects of supplying the European Community with raw materials in sufficient quantities.

Materials availability, either in the short term during critical situations or in the medium/long term due to overconsumption or depletion, is of vital concern to industry and to EC security.

Shortages of critical metal experienced in recent years along with increasing dependance on foreign and unstable sources of supply for certain specific metals have spurred interest in advancing the capability to substitution for these metals.

Substitution can provide industry with the flexibility to deal with specific materials availability problems and in the long term is an important means of coping with shortages.

As essential part in defining the purpose and the scope of these studies was played by the "Working Party" for R & D on materials substitution established by the CREST Subcommittee "R & D on Raw Materials".(1)

First submitted in January 1980, then slightly revised, the documents were prepared under contracts between the Commission of the European Communities and the following organizations :

| | |
|---|---|
| 1. - Société Générale des Minerais<br>- Bruxelles - Belgique; | (Silver) |
| 2. - Bureau d'Information et de Prévision Economique<br>- Paris - France; | (Silver) |
| 3. - Warren Spring Laboratory<br>- Stevenage - United Kingdom; | (Chromium) |
| 4. - Fiat Engineering<br>- Torino - Italia; | (Chromium) |
| 5. - T.N.O.<br>- Delft - Holland; | (Chromium) |

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1) Footnote on next page.

| | |
|---|---|
| 6. - Institut zur Erforschung Technologischer Entwicklungslinien<br>- Hamburg - Federal Republic of Germany; | (Tungsten) |
| 7. - Société d'Etudes et de Conseil en Marketing Industriel.M2i.<br>- Paris - France; | (Tungsten) |
| 8. - Centro Sperimentale Metallurgico<br>- Roma - Italia; | (Tin) |
| 9. - Technische Rijks Hogeschool<br>- Delft - Holland; | (Tin) |

The reports were prepared and submitted while Mr. Ph. Clamen was Chairman of the Working Party assisted by Dr. M. Donato of the Commission staff acting as a scientific secretary. The Commission wishes to thank Mr. Clamen, the national Experts of the Working Party and the authors of these documents for their valuable and kindly cooperation willingly given.

VOLUME I comprises the reports on Silver and Chromium.

VOLUME II comprises the reports on Tungsten and Tin.

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1) Footnote from previous page : Set up by the Resolution of the Council of Ministers of the European Communities of 14 January 1974, the Scientific and Technical Research Committee (CREST) is responsible for assisting the Community Institutions in the field of scientific research and technology development.

COMMISSION OF THE EUROPEAN COMMUNITIES
(Directorate General XII - Research, Science and Education)

# THE SILVER CONSUMPTION IN THE EEC COUNTRIES AND THE POSSIBILITY OF SUBSTITUTION

November 1979

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## Contents

Contents (continued) Pages

Contents (continued) Pages

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# FOREWORD

The purpose of the present study is twofold :

- to determine what would be the economic justification for the EEC to undertake research and development programmes aiming at the substitution of other materials for silver;

- to specify which orientations to give to such R&D programmes to be sponsored by the Commission of the European Communities.

This objective requires a thorough analysis of the silver market at the world level, and more specifically in the EEC countries. Silver economics is studied with respect to :

. the supply structure of silver and its expected evolution toward 1985 (chapter 1);
. the consumption pattern of silver and its possible developments linked to currently ongoing technological progress (chapter 2);
. the silver price dynamics in relation to the status of the precious metal, both as an industrial commodity and as an investment commodity (chapter 3);
. the substitution opportunities of other materials for silver in the presently developed utilizations (chapter 4)

Chapter 5 draws the 1985 picture of the silver market with special reference to the EEC countries, it proposes recommendations for research and development programmes and gives estimates of the silver economies potentially feasible by 1985 and 1990 in the EEC if R&D results are successfully implemented.

The study does not take into account the Centrally Planned Economies (CPE) because of lack in statistical data. Furthermore, net imports of silver from the CPE in the market economy countries, and more especially in the EEC countries, never were a significant element of total supply, and what they will be in the future is highly conjectural.

For the market economy countries, reference is made to the statistics compiled by Handy & Harman. These statistics are detailed for the USA in particular but do not cover systematically all the EEC countries; estimations are provided for those countries or items which are not reported in Handy & Harman's statistics, such estimations are generally based on informations gathered at the occasion of calls. Ireland, Denmark and the Netherlands play a minor role in the EEC silver picture and, considering that no statistics are available for those countries, they are not mentioned individually in the subsequent developments.

Reference to data sources is made in the list of tables and in the bibliography.

The study was carried out by Société Générale des Minerais, Belgium, as pilot, and Bureau d'Informations et de Prévisions Economiques, France, as co-pilot.

The task was assigned as follows :

- for SGM :
  economic evaluation of the world silver market and of the EEC silver supply/demand situation, and 1985 market outlook - this covers chapters 1, 2 and 3 of the study;
- for BIPE :
  technico-economic evaluation of substitution opportunities and identification of research and development objectives - this implied in-depth field survey and resulted in chapter 4 as well as a large contribution to chapter 3

SGM and BIPE jointly worked out chapter 5 on conclusions and recommendations.

# Chapter 1 - SILVER SUPPLY

## 1.1. Production of primary silver

### 1.1.1. Silver reserves and resources

Two factors contribute to the difficulty of evaluating reserves and resources of silver in ores :

- only one third of primary silver occurs as the main product or coproduct component in minerals, the commonest and probably most important silver mineral being argentite ($Ag_2S$); two thirds of the world silver reserves and resources are estimated on the basis of the silver content of copper, lead and zinc deposits, silver being then considered as a by-product of those base metals and the most common association being with lead (galena PbS);
- the evaluation of silver reserves and resources supposes a clear understanding of what "reserves" are as opposed to "resources"; according to the U.S. Geological Survey and the Bureau of Mines, "reserves" mean economically recoverable material in identified deposits, while "resources" include reserves plus hypothetical and speculative deposits as well as identified but currently subeconomic deposits.

Presently recorded resources of silver as evaluated by the U.S Geological Survey, amount to 704,000 mt of Ag, 31 % of which are located in USSR and 62 % in the five leading producing countries : Mexico, Canada, USA, Peru and Australia.

Table 1.1.a. indicates Ag reserves and resources by countries.

Table 1.1.a. 000 mt Ag

| Country | Reserves | Identified subeconomic deposits + hypothetical speculative deposits | Total resources |
|---|---|---|---|
| Mexico | 26 | 84 | 110 |
| Canada | 22 * | 53 | 75 |
| USA | 47 | 131 | 178 |
| Peru | 19 | 37 | 56 |
| Australia | 6 | 11 | 17 |
| USSR | 50 | 168 | 218 |
| Other countries | 20 | 30 | 50 |
| Total : | 190 | 514 | 704 |

* 28 according to the Department of Energy , Mines and Resources Canada.

Ore reserves in the non-communist countries would allow to maintain the 1978 production level for about 17 years.

It is important to keep in mind that future evaluation of Ag reserves will continue to depend largely on the accuracy of Pb, Zn and Cu reserve estimations.

### 1.1.2. Silver metallurgy

Silver contained in Ag, Pb, Cu or Zn concentrates, is refined through cupellation and electrolysis of the Ag-bearing products resulting from the minerallurgy or metallurgy of the base metals. The input to the refining process varies according to the base mineral from which Ag is to be recovered :

- in the case of Ag ores, a Ag bullion grading 50 to 90 % Ag, resulting from the treatment of the Ag ores, enters the refining process;

- in the case of Cu concentrates, Ag is recovered at the end of the Cu refining process from Cu electrolysis slimes which are preliminarily roasted and leached to remove harmful impurities such as S, Sb, Cu;

- in the case of Pb and Zn concentrates, Ag is recovered from a Pb-Ag alloy which results from the desilverization (Parkes process) and Zn distillation of a Pb bullion initially obtained from the melting of Pb concentrates, Ag-bearing Pb residues, Pb-Ag residues from the Zn metallurgy (Pb sulfate).

The main stages of the Ag refining process are as follows :

(1) cupellation, i.e. oxidation of impurities in a molten lead bath (base metals are captured in PbO), yielding. the "doré metal" (98.5 - 99 % precious metals of which max. 8 % Au);
slag to pass back to (1);

(2) melting of the "doré metal" into anodes;

(3) electrolysis either by the Moebius process using vertical anodes in 5 anode cells,
or by the Balbach-Thums process using one horizontal anode per cell (more energy-intensive and less productive);
yielding :
a. slimes (containing 3 to 6 % Ag) and washwaters;
b. used anodes (still containing 8 - 10 % Ag) to pass back to stage (2);
c. Ag crystals;

(4) melting of Ag crystals into ingots, flakes or shots
standard analysis : 999.9 Ag
35 ppm Cu
10 ppm Pb
Au

(5) treatment of slimes and washwaters -
two processes are available :

- integral nitric process;
- sulfuric process or "boiling pot" process (the most commonly used);

the silver nitrate or silver sulphate so obtained is then passed back to stage (2).

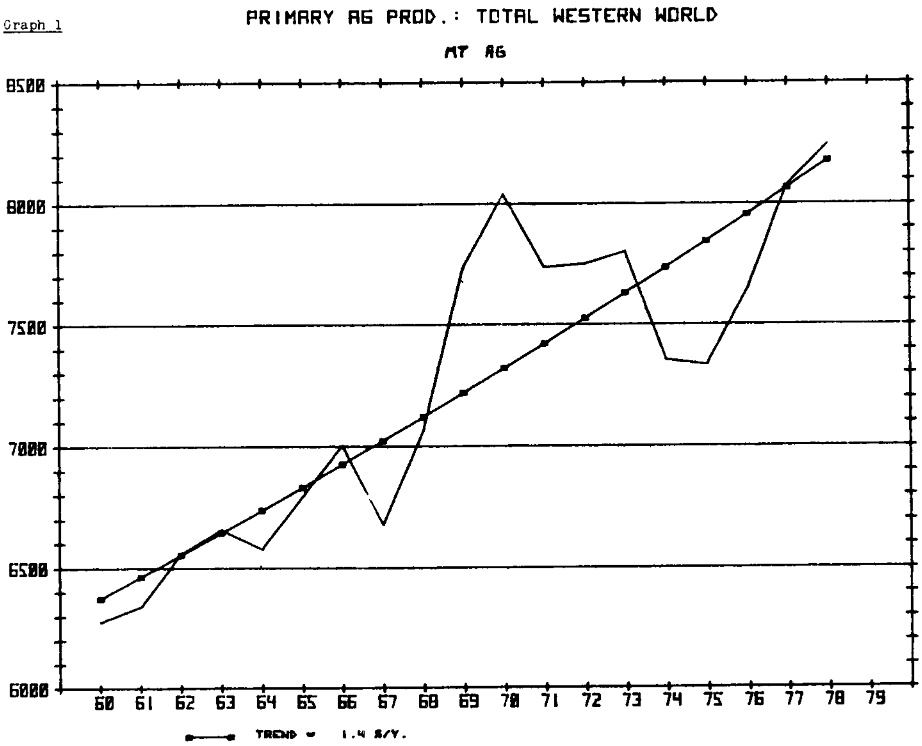
### 1.1.3. Silver mine production

Silver mine production in the non-communist countries in 1977 recovered the 8000 t level it had reached already once in 1970 and preliminary estimates set the 1978 production at a peak of 8,242 t.

Since 1960, silver production is growing at an average annual rate of 1.4 % with ups and downs largely linked to the fluctuations of lead, zinc and copper mine production, as about two thirds of the world primary silver production are produced as a by-product of those base metals.

Graph 1 shows the evolution of silver mine production around its trend over the last 18 years.

Graph 1



2)

Five countries only account for more than 70 % of the total non-communist production : Mexico, Canada, USA, Peru and Australia.

| | Mexico | Canada | US A | Peru | Australia | non-communist world |
|---|---|---|---|---|---|---|
| 1960 | 1,384 | 1,058 | 958 | 958 | 473 | 6,277 |
| 1965 | 1,253 | 1,005 | 1,238 | 1,135 | 538 | 6,793 |
| 1970 | 1,331 | 1,376 | 1,400 | 1,238 | 809 | 8,040 |
| 1975 | 1,182 | 1,235 | 1,087 | 1,058 | 726 | 7,490 |
| 1976 | 1,326 | 1,281 | 1,068 | 1,117 | 779 | 7,646 |
| 1977 | 1,462 | 1,330 | 1,188 | 1,216 | 853 | 8,074 |
| 1978 | 1,661 | 1,241 | 1,182 | 1,236 | 855 | 8,242 |

Source : J Aron - Handy & Harman

Except in Mexico, where an estimated 45 % of the primary silver production results from silver ore mining, lead, zinc and copper ores are the major source materials for silver. The importance of the "by-product" status of silver can be depicted by the correlations between Ag production and base metals productions over the period 1960-1977 :

| | Canada | USA | Peru | Australia |
|---|---|---|---|---|
| Cu | .81 | .57 | .60 | .68 |
| Zn | .89 | .42 | .49 | .90 |
| Pb | .85 | .24 | .65 | .88 |

These correlations measure how closely the evolution of silver production follows the evolution of each base metal. They allow to compare the relative importance of the one or the other base metal as source material for silver within a country, and to outline the differences occurring in this respect from one major producing country to another.

Silver output in the five leading producing countries is growing at a rather low rate of 1.1 % per year, which is significantly lower than the 3 % observed in the base metals production of the same countries (3.1 % for Pb, 3.3 % for Cu, 3.7 % for Zn).

The structure of silver production in the main producing areas is described in the next paragraphs.

## MEXICO

Mexican silver production reached a record level in 1977 with 1,462 t Ag after it had stayed in the 1,150-1,330 t/year range for many years.

The coming up to full production of Las Torres (226 t/year - Cia. Fresnillo) and Lampazos (Minera Frisco) operations accounts for this production increase which should continue in the coming years with the development of new silver deposits encouraged by the new Mexican tax structure and the steady high level of silver prices. Hence, preliminary estimates of 1978 production are in the range of 1,660 t Ag, thus definitely setting Mexico again at the top of the world silver producers.

Mexican silver mine production is expected to reach the 1,700 t-mark by 1979 and to exceed the 1,800 t-level by 1980.

About 55 % of the production is arising presently as a by-product of Cu, Pb and Zn mining; however, the development of recently discovered Ag reserves should lower this share in the future.

More than half of the Mexican silver production originates in three groups of companies :

The Industrias Penoles group, which owns majority shares in La Encantada (Pb-Ag), Cia. Fresnillo (Ag-Pb-Zn-Cu-Cd-Au), Zimapan (Ag-Pb-Zn-Cd-Au-Cu), Cia Minera Las Torres (Ag-Au), Cia. Minera Cedea (Au-Ag), Campana de Plata (Ag) and several other mining units in the prospection stage; Penoles operates a lead-silver refinery at Torreon, through its subsidiary Met-Mex Penoles; production reached a record level of 978 t Ag in 1977, including foreign and domestic toll-treated metals.

- The Industrial Minera Mexico group, which operates several base metals mining units, either directly (Charcas, San Martin, Santa Eulalia, Taxco), or through subsidiaries (Minerales Metalicos del Norte operating Tecolote, Velardena project, Santa Barbara, and Zinc de Mexico operating Parral, Plomosas, Inguaran); in 1977, silver contained in ores milled (Cu, Pb, Zn, Ag) amounted to 259,918 kg and the Pb-Au-Ag refinery at Monterrey produced 522,288 kg Ag from IMM materials and domestic and foreign toll-treated materials.

- The Minera Frisco group, which holds 100 % interest in Minera San Francisco del Oro (89 t Ag in 1977) and 68 % in Minera Lampazos which, in 1975, reopened the Lampazos mine, idle for about 60 years, and plans to raise production from 150,000 t ore/year to possibly 300,000 t ore/year; the Lampazos ore contains an average of 16 oz Ag/t.

## CANADA

Canadian silver production amounted to 1,314 t of recoverable Ag in 1977. More than 50 % of the silver produced is supplied as a by-product of copper ores and this share is expected to grow in the future, especially in connection with the growth of Texasgulf Kidd Creek's production. In 1977 silver production derived from the following source materials (°) :

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(°) Source : Silver-cobalt mines and silver-lead-zinc mines, 1977 - Statistics Canada - Catalogue 26-216.

| | |
|---|---|
| Cu-Au-Ag ores | 53 % |
| Ag-Pb-Zn ores | 39 % |
| Ag-Co ores | 3 % |
| Ni-Cu ores | 4.5 % |
| others | 0.5 % |

Table 1.1.b. details the main sources of production with reference to 1977 tonnages. It appears from this table that about 18 % only of the total production arises from Ag ores or from base metal ores where Ag accounts for the major part of the value; Teck Corp., Terra Mining, United Keno Hill Mines and Echo Bay Mines are the main such producers. Three companies only account for about 54 % of the total production, Texasgulf Kidd Creek mine being the largest single Ag producing unit in Canada.

Table 1.1.b. - Main primary silver producers in Canada

| Companies | 1977 production kg Ag contained in concentrates | Mines |
|---|---|---|
| Brunswick Mining & Smelting | 133,061 | N°12-N°6 Mines, New Brunswick Pb, Zn, Ag |
| Cominco Ltd. | 292,248 (*) | Sullivan, B.C. - Pb, Zn, Ag |
| Cyprus Anvil Mining | 37,600 | Vangorda Creek, Yukon - Pb, Zn, Ag |
| Falconbridge Copper Ltd. | 21,536 | Opemiska, Quebec - Cu, Ag<br>Lake Dufault, Que.- Cu, Zn, Ag |
| Hudson Bay Mining & Smelting | 24,533 | Flin-Flon and Snow Lake, Manitoba - Cu, Zn, Pb, Ag |
| Inco | 66,873 | Sudbury, Ont. - Ni, Cu, Ag |
| Mattabi Mines | 83,924 | Sturgeon Lake, Ont. - Zn, Cu, Pb, Ag |
| Noranda Mines | 49,175 | Geco, Ont. - Cu, Zn, Pb, Ag |
| Texasgulf Canada | 277,568 | Kidd Creek, Ont.- Cu, Zn, Ag<br>Nanisivik, Baffin Island - Zn, Pb, Ag |
| Western Mines | 28,422 | Lynx and Mica, B.C. - Cu, Zn, Pb, Ag, Au |

(*) refined metal, including Ag sold in concentrates and intermediate products.

| Companies | 1977 production kg Ag contained in concentrates | Mines |
|---|---|---|
| Teck Corporation | 42,021 | Silverfields and Beaverdell, B.C. - Ag |
| Terra Mining | 46,043 | Silver Bear and Norex, Northwestern Territories - Ag |
| United Keno Hill Mines | 86,595 | Galena and Keno Hill, Yukon - Ag, Pb, Zn |
| Echo Bay Mines | 67,468 | Port Radium |
| Total mine production : | 1,313,684 | as reported by Statistics Canada. |

There are only four silver bullion producers in Canada :

- Canadian Copper Refiners, wholly owned subsidiary of Noranda, operates a copper refinery in Montreal, Quebec, and produced 683,841 kg Ag in 1977. Canadian Copper Refiners processes the production of Hudson Bay and Mattabi Mines.
- Cominco's silver refining capacity at Trail, B.C., reaches 370,000 kg Ag per year.
- Brunswick Mining and Smelting Corp. has a bullion production at its Belledune lead smelter. The tonnage produced in 1977 was 107,556 kg Ag
- Inco operates a precious metals recovery plant at its Copper Cliff copper refinery.

The Canadian primary production of silver will continue to largely depend on base metals production, especially Cu and Zn. Two new productions should come on the market in the early 80's :

- from the Sam Goosly copper-gold-silver deposit, Equity Silver Mines, scheduled to start up in mid-80, with an average annual production of 23,400 kg Ag;

- from the Detour River copper-zinc-silver deposit, Selco Mining Corp., where the average Ag content of the ore is estimated at 1.05-1.20 oz Ag/ton, scheduled for mid-80.

It should, however, not be expected that the overall growth of the primary Ag production in Canada could break, over the next five years, the maximum reached in 1973 (1,477 t Ag) when the production of base metals was at exceptionally high levels.

USA

The US by-product silver output in 1977 was affected by lower base metals productions as a result of strikes, mainly at copper operations, and of low utilization rates of mining capacities in view of the Cu, Pb and Zn market oversupply position. On the contrary, silver production at silver mines sharply increased with two newly opened mines (Delamar and Day) operating at near capacity. Total primary silver mine production amounted to 1,188 t, an overall 11 % increase over the 1976 production.

40 % of the US silver production is located in the Coeur d'Alene mining district, Idaho. The Galena and the Sunshine mines, Idaho, operated respectively by Asarco and the Sunshine Mining Company, are the two largest single silver mines in USA; they produced 115,145 and 100,320 kg Ag in 1977.

Among the 25 mines which account for about 85 % of the US production, six are operated primarily for Ag, ten are copper mines and nine are Pb and/or Zn mines.

Table 1.1.c. reviews the main primary silver producers in the USA with reference to the 1977 production figures.

Table 1.1.c. - Main primary silver producers in the USA

| Companies | 1977 production kg Ag contained in concentrates | Mines |
|---|---|---|
| Anaconda | 112,026 | Twin Buttes and Carr Fork Cu-Mo mines |
| Asarco | 189,203 | from Galena and Coeur, Idaho Ag, Cu |
| | 32,424 | contained in Pb-Zn ores milled |
| | 29,756 | contained in Cu ores milled |
| Bunker Hill | 48,970 | from Bunker Hill, Crescent, Star (70 % interest) - Ag, Pb, Zn |
| Cyprus Mines | 36,049 | from Bagdad copper mine, Arizona |
| Day Mines | 56,907 | from Daycock and Graycock, Idaho - Pb, Zn, Ag |
| Delamar Silver Mine | 25,274 | from Delamar, Idaho - Au, Ag |
| Hecla Mining | 123,665 | from Lucky Friday - Ag, Pb, Zn, Star - Ag, Pb, Zn (30% int.), Sunshine - Ag (33% interest), Lakeshore - Cu (closed in September 1977 for non-profitability) |
| Homestake Mining | 63,669 | from Bulldog, Col. - Ag, Pb |
| Kennecott Copper | 100,705 | from copper mines (Chino - Ray - Wah - Nevada) |
| | 39,352 | from Pb-Zn operations (Ozark, Tintic) |
| Phelps Dodge | 55,395 | from Cu mines in Arizona and New Mexico |
| Sunshine Mining | 67,263 | from Sunshine (excluding Hecla's share) |

Primary silver production will continue to develop partly in accordance with the progress of Cu, Pb and Zn mine production, partly in accordance with new developments in silver mining, such as the opening of a second open pit at the Delamar silver mine by the end of 1979, the exploitation from 1979 to 1983 of the rich gold-silver deposit of Buckhorn, Nevada (Bar Resources), the start-up by 1981 of Asarco's Troy copper-silver mine with an annual production rated at 130 t Ag, the expansion in 1982 of the Sunshine mine (+ 68 t Ag yearly).

Refined production of silver from primary sources in USA is accounted for by about 25 refineries; it amounted to 1,400 t in 1977, an exceptionally low level as compared with the average of the last five years : 2,000 t a year with a peak of 2,350 t in 1973. The largest primary Ag refiner is Asarco with a capacity of more than 1,800 t Ag per year at Amarillo, Texas. Table 1.1.d. lists the four main Ag refineries in the USA (with a mention of the Government refinery).

Table 1.1.d. - Main primary silver refineries in the USA

| Company | Location | 1977 production |
|---|---|---|
| Asarco | Amarillo, Texas<br>capacity :<br>1,865 t Ag/year | 1,041,376 kg Ag<br>from Asarco's copper and lead bullion (14 %), purchased material (85 %), toll-treated material (1 %) |
| Bunker Hill | Kellogg, Idaho<br>capacity :<br>370 t Ag/year | 232,654 kg Ag<br>50 % from own sources |
| Kennecott | Baltimore, Maryland | 100,705 kg Ag |
| Phelps Dodge | El Paso, Texas<br>Laurell Hill, N.Y. | 86,530 kg Ag<br>(100,650 kg Ag in 1978), including toll-treated materials |
| US Assay Office | New York, N.Y. | |

US primary silver refineries cannot be supplied entirely by domestic Ag ores and concentrates; the supply must therefore be supplemented by imports. These imports mainly come from Canada, Honduras, Australia, Peru and Mexico. Imported Ag largely supplies the East Coast refineries.

The following table enables to compare the evolution of the US primary Ag mine production, imports of Ag ores and concentrates and primary refined production in the 70's.

| | Ag mine production t Ag | Imports of Ag ores and concentrates (t Ag - code 2850120) | Refined Ag production t Ag |
|---|---|---|---|
| 1970 | 1,400 | 983 | 2,532 |
| 1971 | 1,293 | 578 | 2,137 |
| 1972 | 1,163 | 1,168 | 2,410 |
| 1973 | 1,158 | 1,382 | 2,345 |
| 1974 | 1,052 | 1,147 | 1,969 |
| 1975 | 1,087 | 725 | 1,869 |
| 1976 | 1,068 | 557 | 1,692 |
| 1977 | 1,188 | 574 | 1,400 |

Apart from inventory effects which cannot be considered here because of lack of information, imports over the last eight years accounted for 43 % on the average of refined output. The expected development of mine production over the next five years would not bring forth any major change in this picture. Even the huge output from Troy should not drastically reduce the need for imported ores and concentrates since there is still a large refining capacity available at Amarillo (Asarco) and, with Sunshine intending to integrate its operations up to the refinery stage, some capacity will become available at the refineries which ensured custom treatment of the Sunshine ores.

## PERU

In 1977, Peruvian silver mine production amounted to 1,183 t, this production level is quite representative of the levels reached during the 70's. About 85 % of the silver production is linked to copper and lead mining, with more than 70 % of the total Peruvian output arising from Centromin's mines.

Centromin's production in 1977 amounted to 857,596 kg Ag from the Cerro de Pasco, Casalpaca, San Cristobal, Cobriza and Morococha mines; refined silver is produced at the lead and copper refinery La Oroya and about 600 t Ag were produced in 1976. Cie. des Mines de Huaron is the other base metals producer with a significant silver production, although much smaller than Centromin's : 51 t of silver were contained in copper and lead concentrates produced in 1977.

The production capacity of silver mines can be estimated at 180 t Ag per year, the main producer being Cia. de Minas Buenaventura. It operates four mines and plans to double the capacity of one of them, Uchuachuaca, raising it from 28 t Ag/year to 60 t Ag/year. Almost the entire production of silver mines is sold to Minero Peru and exported as concentrates.

Refined silver production in Peru essentially originates in the refining of copper and lead concentrates at La Oroya (650 - 690 t Ag per year) and the toll-treatment of lead concentrates by Penoles at its Torreon plant in Mexico (110 - 120 t Ag/year).

Silver production in Peru is expected to grow in the future, with reference to :

- the development of production at existing copper and lead-zinc mines (i.e. Cobriza expansion);
- the start-up of new base metals operations with prospects of silver values contained in base metals concentrates, such as the Toromocho Centromin's project scheduled for 1982-83, including an anode sludge processing plant which could yield 60 t Ag per year, or the Antamina Geomin-Mineroperu project scheduled for 1983-84, based on a Cu-Zn-Mo deposit with Ag content estimated at 15.5 g Ag/t;
- the expansion of operations at silver mines such as planned by Buenaventura.

## AUSTRALIA

Silver mine production in Australia is essentially a by-product of lead and zinc mining. The largest producer is the MIM Holdings : in 1977, 2.4 million tons of silver-lead-zinc ores grading 212 g/t Ag were extracted from the Mount Isa mine, yielding 410 t Ag contained in lead concentrates. Reserves at Mount Isa are large enough to ensure production over at least 20 years from now (56 million tons ore grading 150 g/t Ag) and the nearby Hilton mine contains a further 37 million tons Pb-Zn-Ag ores assaying 180 g/t Ag

The Mount Isa lead concentrates are refined at the Northfleet Refinery in the United Kingdom; this refinery reported a production of 328 t Ag in 1977.

MIM Holdings silver production represents more than 50 % of the total Australian silver output and is the world largest single mine production of silver.

There are two other significant silver producers in Australia :

- Australian Mining and Smelting, a 100 % subsidiary of Conzinc Rio Tinto Australia, which, in 1977, produced 122 t Ag in lead concentrates from its New Broken Hill Associated mine;
- North Broken Hill Holdings, whose production fluctuates between 90 and 110 t of silver per year (contained in lead concentrates); the concentrates are sold to BH Associated Smelters, Port Pirie, which produced 188 t of refined silver in 1977.

Smaller tonnages are recovered as a by-product of copper, for instance at Peko Wallsend Mount Morgan smelter (11 t in 1977, 18 t in 1976), and at Mount Lyell Mining (2.5 to 3.5 t Ag/year in copper concentrates).

Australian silver production is expected to be maintained above the 800 t level during the next five years. The Woodlaw Pb-Zn-Cu-Ag operations, in which Australian Mining & Smelting has a 33 % interest, started up by the end of 1978; silver production should reach 27 t per year in lead concentrates. The silver values of the Teutonic Bore Cu-Zn deposit (50 g/t Ag), presently explored by a MIM-Selcast joint venture, and the silver values of the Que River Pb-Zn-Cu-Ag deposit (107 g/t Ag) could guarantee the progress of the Australian silver mine production in a more distant future.

## EEC COUNTRIES

The total European primary silver production amounted to 660 t in 1977, i.e. 8 % of the Western World production. The largest contributors to the European production are : Yugoslavia (146 t Ag), Sweden (159 t Ag) and Spain (100 t Ag); the EEC countries altogether provide around 200 t Ag per year.

There are no silver ore deposits in Europe and the whole primary Ag production refers in fact to the Ag contained in copper, lead and zinc concentrates produced.

The following table reviews the EEC mining operations with Ag-bearing base metals production.

Table 1.1.e.

| Countries with 1977 Ag production | Company | Mine location | Remarks |
|---|---|---|---|
| Denmark (Greenland)<br>16.2 mt Ag | Greenex A/S (Cominco) | Black Angel, Marmorilik | Ag contained in<br>Pb conc. 400 g/t<br>Zn conc. 12.4 g/t |
| France<br>89.8 mt Ag | Peñarroya | Saint-Salvy | Ag contained in<br>Zn conc. 516 g/t |
| | | Largentière | Ag contained in<br>Pb conc. 1466 g/t<br>Zn conc. 311 g/t |
| | | Les Malines | Ag contained in<br>Pb conc. 1022 g/t<br>Zn conc. 137 g/t |
| | Société Minière de Corrèze | Les Farges | Ag contained in<br>Pb conc. 1200 g/t |
| West Germany<br>33 mt Ag | Preussag | Bad Grund | Ag contained in<br>Pb conc. 903 g/t |
| | | Rammelsberg | Ag contained in<br>Cu conc. 673 g/t<br>Pb conc. 401 g/t<br>Zn conc. 123 g/t |
| Italy<br>37.5 mt Ag | Ammi Sarda | several Pb, Zn, Ag orebodies | |
| | Piombo Zincifera Sarda | id. | |
| | Pertusola (Peñarroya) | Salafossa | Ag contained in Pb, Zn concentrates |
| Ireland<br>26.5 mt Ag | Irish Base Metals | Tynagh | Ag contained in Pb, Zn and mixed concentrates |

## OTHER PRODUCING COUNTRIES

Since 1970, smaller productions have contributed to the continuation of the world silver output growth :

- Indonesia doubled its annual silver output in 1973 with the opening of the Ertsberg copper mine (P.T. Freeport Indonesia), bringing it from an average annual output of 10 t Ag to 19 t in 1973, and maintaining production at around 24 t during the last five years.
- Silver production in South Korea rose from about 20 t in the 60's to 47 t in 1970 and 64 t in 1977.
- Morocco reached a peak level in 1972-73 with 105 t, coming from 27 t in 1969 and returning to 10 t in 1977.
- Silver production in Chile has been regularly increasing since 1972 and reached a record level of 261 t in 1977, mainly in connection with Cu production.
- New silver productions appeared on the market :
  - . in 1971 from Bougainville copper mine, Papua New Guinea (47 t Ag contained in Cu concentrates in 1977);
  - . in 1973 from the Greenex Marmorilic Pb-Zn mine in Greenland (16 t in 1977);
  - . in 1975 from the Au-Ag Pueblo Viejo mine, Rosario Dominicana, Dominican Republic (42 t in 1977).

Over the next five years, silver production growth outside the five big producing countries will partly result from :

- a doubling of capacity at the El Mochito mine, Rosario Resources, Honduras, which presently supplies around 100 t Ag per year to the world market;
- the start-up of the Varovaca mine in Yugoslavia, expected to produce 25 t Ag per year, along with Pb concentrates, Zn concentrates and barytes;

- the expansion of operations at the Au-Ag mine of Emperor Mines, Fiji;
- the development of copper production in the Philippines which was recently encouraged by the supply opportunities on the Chinese market (silver contained in copper concentrates produced in 1977 amounted to 50 t);
- the start-up in Spain of three large operations with a significant by-product silver output :
  - . 60 t in Pb and Cu concentrates at the Aznacollar mine, Andaluzas de Piritas, as from 1979;
  - . 22 t in Pb, Zn and Cu concentrates at the Huelva mine, AIPSA, early in 1980;
  - . 15 t in Pb and Zn concentrates at the Rubiales mine, Exminesa, in 1980;
- the start-up of operations at the Black Mountain Pb-Zn-Cu-Ag deposit in South Africa, during the first quarter of 1980; Ag production would amount to 120,000 kg/year as a by-product of Pb, Zn and Cu concentrates;
- the development of the El Indio Cu-Au-Ag deposit by Minera San Jose, a subsidiary of St.Joe Minerals, in Chile, with an expected production of about 15,500 kg Ag bullion per year, starting in 1982.

### 1.1.4. The outlook of primary silver production

1985 primary silver production of the non-communist countries will certainly exceed the 9000-t level. Several projects are under way in the main producing countries and significant new productions should come on the market from smaller producers such as Honduras, South Africa, Spain.

Section 1.1.3. mentioned those projects giving some details, and their impact on the total primary silver production is edtimated in table 1.1.f. This table proposes, in fact, three estimates of the western world 1985 primary silver production :

a. taking into consideration the existing projects and the 1978 utilization rate of Cu, Zn and Pb mine capacities;

b. taking into account the existing projects and a maximum utilization rate at the base metals mines;

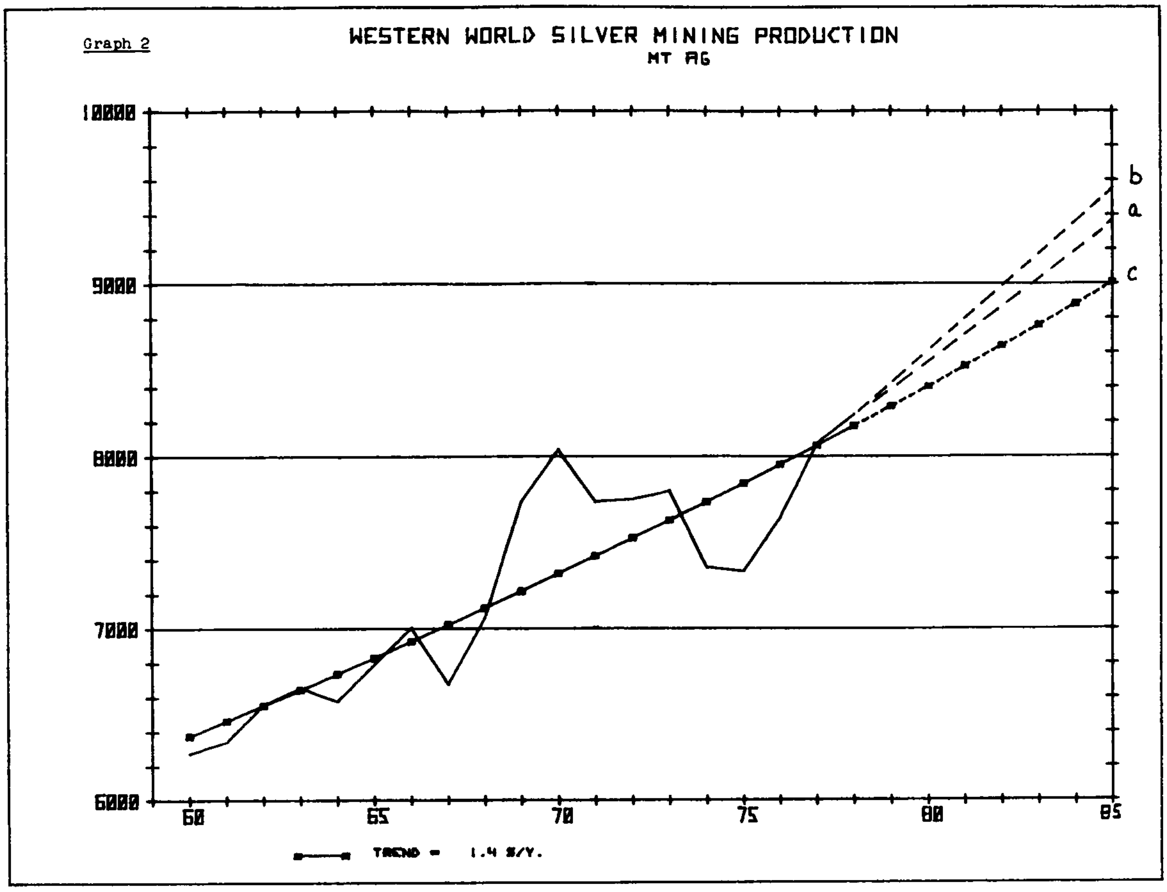
c. extrapolating the long-term trend of 1.4 % per year of total production.

Table 1.1.f. - 1985 primary silver production

(mt Ag)

| | 1978 | 1985 | | |
|---|---|---|---|---|
| | | a | b | c |
| Mexico | 1,661 | 1,850 | 1,900 | - |
| Canada | 1,241 | 1,400 | 1,400 | - |
| USA | 1,182 | 1,500 | 1,600 | - |
| Peru | 1,236 | 1,350 | 1,350 | - |
| Australia | 855 | 870 | 870 | - |
| Other non-communist countries | 2,067 | 2,400 | 2,430 | - |
| Total western world : | 8,242 | 9,370 | 9,550 | 9,007 |

Mexico would remain the leading producer and the USA would return to the second position. The share of the five major producers in the total would remain as it is now, i.e. about 75 %. Graph 2 positions the above forecasts towards past realizations.



Graph 2

WESTERN WORLD SILVER MINING PRODUCTION
MT AG

## 1.2. Above-ground supplies of silver

Above-ground supplies of silver are of four kinds :

- Indian silver, accumulated over centuries in private hands as a means to preserve and increase wealth; it is in the form of personal ornaments and temple artifacts which are collected in the villages and melted in impure bullions available for export;

- industrial scrap, including old scrap obtained after end-products have been used and discarded and new scrap generated during the manufacturing operations.

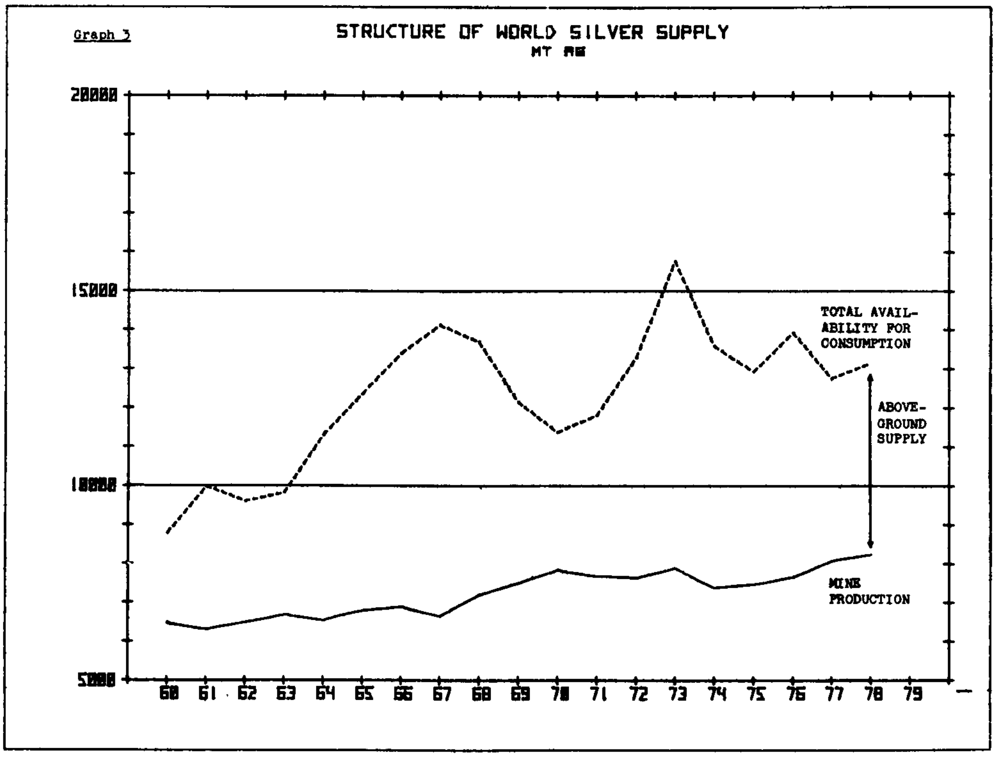
- demonetized coins resulting from recovery programmes conducted by governments in many countries of the world;
- inventories held by the industry, the Exchanges, the national banks and the governments.

In 1978, total above-ground supplies of silver amounted to 5,074 t Ag, distributed as follows :

| Source | Tonnages mt Ag | % of total |
|---|---|---|
| Indian silver | 1,477 | 29.1 |
| industrial scrap | 2,613 | 51.5 |
| demonetized coins | 435 | 8.6 |
| estimated inventories changes | 549 | 10.8 |
| Total : | 5,074 | |

Source : Handy & Harman.

Over the 70's, above-ground supplies of silver covered, on the average, 40 % of the world total needs of silver. It has always been a highly significant source of metal because of the fundamental deficit of primary supply as compared with consumption as is depicted in graph 3.


Graph 3

STRUCTURE OF WORLD SILVER SUPPLY
MT AG

The following sections develop the specifics relating to each of the above-ground supply sources.

### 1.2.1. Processing of secondary sources of silver

Secondary sources of silver are highly diversified as far as grades and physical and chemical properties are concerned. This very complex nature of secondary feed justifies the existence of complicated and highly flexible refining flowsheets involving fire as well as chemical processing The complexity and variety of the Ag scrap refining flowsheets make it difficult and somewhat useless to go into their extensive description; however, considering the relative importance of photography scrap materials in the total Ag recovery from secondary sources, the major steps in processing such scrap are especially reviewed in appendix 1.

Research in the field of Ag scrap processing is being pursued continuously in two directions :

- Improvement of existing recovery methods to achieve higher recycling rates at a lower cost; one example in this respect is the development of an enzymatic recovery process to be applied to developed films usually treated by incineration, the enzymatic process is less polluting, more efficient and economical and Ag extracted reaches a higher purity level than in the conventional incineration process.
- Development of new processes to recover Ag where it is left discarded up to now; the price level of Ag is, in this respect, an important incentive to recycling efforts, but other preoccupations, such as pollution, may also be determinant in the search for new processes; for instance, a federal law in the U.S.A. will tolerate a maximum content of 1 ppm of heavy metals in sewage as from 1983, recovery methods should therefore be developed in due time to comply with this rather severe regulation.

An important phase of Ag recovery from the many different products where it has been used, is the collection, consolidation and shipment of scrap materials to the processing units. These preliminary steps are of crucial importance to the total amount of silver which can be effectively recycled.

The most efficient organization in this respect certainly concerns the products of the photography industry.

Improved collection systems could certainly increase the supply of secondary Ag from other industrial products. However, once again, the price level of Ag is the basic incentive to a more efficient collection of Ag scrap.

### 1.2.2. Indian silver

The importance of India on the silver market results from the huge amounts of precious metals accumulated over centuries in private hands, silver being traditionally considered as a means to accumulate and preserve wealth, especially in anticipation of starvation periods.

Indian silver supply is therefore highly volatile since the owners of this huge above-ground resource, farmers and villagers and the smaller class of wealthy individuals, are quite sensitive to the two elements which fundamentally justify the possession of silver : its buying power and hence its price, and the changes in economic conditions largely linked to the quality of the harvest of the past year, which determines the development of dearth, or not, during the subsequent year.

Silver exports were prohibited up to 1974 in order to preserve foreign exchange, but a lot of smuggling was going on, especially through the Middle East countries (Abu Dhabi and Oman). The situation induced the Government to officially authorize silver exports in February 1974 and a tighter control was established in August 1976 when it was decided to channel all the silver sales through the State Trading Corporation of India (STC). The STC exports silver from Bombay, New Delhi, Calcutta and Madras, within the limits of the annual quota specified at the beginning of each fiscal year starting April Ist.

The STC does not publish any statistics on the sales and all the informations regarding such sales should be considered with great care; they are gathered in the following table; they are mainly compiled from Handy & Harman's annual review :

**Table 1.2.a.**

| FY ending March 31st. | Tonnages | | Value | | | |
|---|---|---|---|---|---|---|
| | Exports mt | STC quota mt | Mln Rs | Mln $ | ¢/oz. | NY price ¢/oz |
| 1973 - 74 | n.a. | - | 65 | 8 | | 255.8 |
| 1974 - 75 | 640 | - | 800 | 96 | 466.5 | 470.8 |
| 1975 - 76 | $1,217^e$ | - | n.a. | - | - | 441 9 |
| 1976 - 77 | 1,655 | 1,600 | 2,140 | 256 | 481 1 | 435.3 |
| 1977 - 78 | 645 | 1,000 | 853 | 102 | 491.9 | 462.3 |
| 1978 - 79 | 724 | 1,000 | 1,100 | 134 | 575 7 | 540.1 |

e = estimated.

The European countries seem to attract the bulk of Indian silver shipments. Furthermore, it is interesting to note that among the EEC countries, the United Kingdom and France are the main importers, with some tonnages going to West Germany and Italy. Statistics do not record any import of Indian silver in the Netherlands, and Belgian statistics do not even detail silver imports at all.

Table 1.2.b. - Silver imports from India in the EEC countries

(000 kg)

| | Belgium | France | W.Germany | Italy | Netherlands | U.K. |
|---|---|---|---|---|---|---|
| 1974 | n.a. | 100.7 | - | 0.8 | - | $250^e$ |
| 1975 | | 299.3 | 4.8 | 52.9 | - | 890 |
| 1976 | | 183.4 | 144.2 | 20.0 | - | 890 |
| 1977 | | 445.6 | 22.0 | 2.5 | - | 159 |
| 1978 | | 230.5 | 15.0 | - | - | 351 |

Sources : Import-export national statistics -
Ref. 71 05 010 to 71 05 030.

e = estimated.

In early 1979, the Indian Government decided to temporarily stop the exports of silver during fiscal year 1979-80 and it is understood that such a decision results from political rivalries only. This makes the future of silver supply from India rather ambiguous and difficult to outline although above-ground reserves are estimated at 78,000 mt, at least, in the form of private ornaments, temple artifacts and, to a lesser extent, bullion.

There is nothing to expect from Indian silver mine production which is negligible and essentially results as a by-production of lead and zinc refining by Hindustan Zinc : 5,698 kg of refined Ag were produced during fiscal year 1976-77 and 11,419 kg during fiscal year 1977-78.

Indian silver consumption for industrial uses reached 622 t in 1978, a record level as compared with the average yearly consumption of 482 t over the 70's. The evolution of the consumption up to the mid 80's should, however, not endanger the theoretical economic availability of Indian silver supply on the world market.

Two factors seem determinant for the appraisal of the Indian silver exports :

- the policy of the State Trading Corporation, and, within the limits imposed by STC,
- the silver price which is the prominent economic incentive to silver releases by private owners, provided domestic economic conditions do not counteract this influence.

### 1.2.3. Industrial scrap

There are neither reliable nor comprehensive statistics on the quantities of new and old silver scrap generated, reprocessed and re-used by the industry. The Handy & Harman's estimation of the world industrial silver scrap supply is the difference between world consumption and silver supply from all identified sources (mines, demonetized coins, Indian exports, silver stocks). According to this evaluation, industrial scrap got an increasing share of the total silver supply during the 70's :

Table 1.2.c. - World industrial silver scrap supply

| | mt Ag | % of total secondary silver | % of total silver supply |
|---|---|---|---|
| 1970 | 1,089 | 31 | 10 |
| 1971 | 871 | 21 | 7 |
| 1972 | 1,400 | 25 | 11 |
| 1973 | 1,866 | 24 | 12 |
| 1974 | 2,053 | 33 | 15 |
| 1975 | 2,271 | 42 | 18 |
| 1976 | 2,364 | 38 | 17 |
| 1977 | 2,488 | 53 | 20 |
| 1978 | 2,613 | 53 | 20 |

Source : Handy & Harman.

A rough estimation would localize about 60 % of the total industrial silver scrap supply in the U.S.A , 5 to 10 % in Japan and 30 to 35 % in Europe and the rest of the world. Such a distribution is at least compatible with the consumption pattern in those countries and with the true fact that the extent of recycling of any material is a direct function of technological and industrial progress.

Total industrial scrap includes old scrap arising after the end-product has been used and discarded, and new scrap generated during the manufacture operations. The economy of scrap recovery largely depends on the silver content of the scrap material, the price of silver and the cost of the recovery treatment which may require complex chemical or electrochemical processes according to the nature and the origin of the scrap material (ref. section 1.2.1.)

Photography and printing industries are probably the largest generators of silver scrap in the form of ash from burnt films and papers, cartridges, photography wastes, sludges, flakes, used developer solutions. Recovery processes are rather complex and require stringent controls to avoid Ag losses and pollution (ref. appendix 1 ).
Ag recovery occurs at different levels in the photography industry and is a key factor to ensure the long-term expansion and profitability of the industry. The large producers are therefore maintaining constant efforts of research to improve recovery; hence, silver contained in waste waters rejected by photochemical plants, photographic laboratories and film duplication installations, is also recycled so as to recover its silver content or at least part of it and to comply, at the same time, with antipollution regulations.
In-house processing of used developer solutions is expanding at the consumer level, especially in hospitals, laboratories and printers where X-ray films are extensively used. Appropriate equipments are generally installed and maintained by the film producers themselves or by specialized recycling companies.
In-house processing is economically viable if internal consumption allows a monthly recovery rate of 1.4 to 2.2 kg Ag, depending on the process used (without or with recirculation, cfr. appendix 1 , point 2). However, more stringent antipollution regulations as well as higher silver price could lower the above viability limits. In this respect, several projects of antipollution legislation are expected to come up in the near future in European countries, especially in the United Kingdom and France; these projects would fix limits to the heavy metals content of wash waters which should thus be more extensively processed prior to being discarded.
Specific data concerning in-house processing of developer solutions are available for France. It is estimated that 80 % of medical laboratories are equipped for Ag recycling

and reach a 70 % recovery rate on the average, yielding a total of about 60 t Ag per year. In-house processing is less developed in industrial laboratories and at printers, where the equipment rate ranges between 40 and 50 %. Potential recovery from this consuming sector could reach 100 t Ag per year but, presently, it amounts to about half that quantity.

As far as solid photography scrap is concerned, the main sources are the developed X-ray films, graphic art films and new scrap generated by the photography industry. At the EEC level, about 25 to 30 % of these materials are recovered for Ag recycling, yielding around 100 t Ag per year. Improved collection systems could more than double this tonnage, even if we consider as a limitating factor the delay in recovery incurred through the archival preservation of some of the developed films, especially in hospitals. Once again, the recovery rate of used films is higher in medical applications than in industrial applications.

Significant quantities of silver scrap are produced during the primary production of solders, brazing, silver alloys, silver-bearing batteries, electric contacts, wires, condensers, electronic devices, silver-plated bearings and containers. Much secondary scrap is also generated through the use of these materials. Scrap of this nature covers a wide range of silver content, it is not always recoverable or directly re-usable because silver is generally mixed or alloyed with other metals (Au, Pd, Cd, W, Cu, Zn, Mg, Ni); therefore, its collection, consolidation and re-processing often depend on the combined value of these metals, rather than on the sole silver value. The use of Ag plating in electric contacts and, more generally, a lesser use of silver in its different applications, make silver recycling much less easy and much less economical . In this respect, some electronic scraps are exported to Hong Kong and Panama, where dismantling can be done more economically and where zero taxation allows to reach a higher added value.

The jewelry and silverware industries generate sizeable tonnages of scrap, either liquid or solid. Liquid scrap occurs in the silver plating segment of the industry : spills of the silver rich electrolytes, dilute wash solutions, spent electrolytes. These materials are generally collected together as a mill waste usually containing 260 ppm Ag; it is then processed to recover silver as a chloride or as metal. Solid scraps chiefly result from sterling ware in many different forms, with widely varying Ag content (trimmings, turnings, punchings, fumes, dusts, drosses from melting and casting, ...). Pure scraps are directly remelted, assayed and re-used, while the others are melted as impure bullion and sent to a precious metal refinery.

Silver can also be recovered from spent catalysts discarded by the chemical industry, from various kinds of residues produced by the glass and the pottery industries, from amalgams and dental alloys used in dentistry.

The future availability of industrial silver scrap will largely be linked to both technological and economic factors :

- technological progress should improve the efficiency of recycling processes and allow Ag recovery where it was not technically feasible before;
- antipollution concern will compel to increase recovery, especially if governments set up specific regulations in this respect; legislation on this matter si already well advance in the U.S.A. and silver recycling will certainly benefit from the enforcement in 1983 of a federal law imposing a maximum of 1 ppm heavy metals in waste waters; in the U.K., legislative authorities are working on the subject and in France, the "Agences de Bassin" are aiming at similar rules;
- high silver price will enhance the economic justification of recycling, improve the profitability of recovery processing itself and encourage the development of new recycling processes.

### 1.2.4. Coin melt

World silver supply of demonetized coins amounted to 435 t only in 1978, which compares poorly with the peak level of 1,710 t reached in 1976. Coin melt has always been a source of silver supply but the tonnages offered on the market widely varied from one year to another because silver recovery from coins largely depends on politico-economic decisions taken by the national monetary authorities and on the sensitivity of private holders to silver prices.

During the 70's the contribution of demonetized coins to world silver supply developed as follows :

Table 1.2.d.

| | mt Ag | as a percentage of total secondary supply | as a percentage of total Ag supply |
|---|---|---|---|
| 1970 | 778 | 21.9 | 6.8 |
| 1971 | 622 | 15.1 | 5.3 |
| 1972 | 467 | 8.2 | 3.5 |
| 1973 | 1,213 | 13.4 | 7.7 |
| 1974 | 1,462 | 23.6 | 10.8 |
| 1975 | 1,089 | 20.0 | 8.4 |
| 1976 | 1,710 | 27.3 | 12.3 |
| 1977 | 715 | 15.3 | 5.6 |
| 1978 | 435 | 8.9 | 3.3 |

Source : Handy & Harman.

Coin recovery programmes are regularly set up by governments to convert small quantities of coins into bullion to be sold on the market. Large scale programmes contributed significantly to the silver supply in the past :

. in 1947, the United Kingdom demonetized silver coinage to repay reconstruction loans granted by the U S.A.;
. during the 60's, the U.S. Treasury demonetized 90 % of silver coins to face rapidly growing industrial demand;
. the demonetization of Australian coins procured 2000 t of Ag 50 - Cu 40 - Ni 5 - Zn 5 alloy which was refined partly in the U.K. by Johnson Mathey, partly in West Germany by Norddeutsche Affinerie;

. in 1976, West Germany demonetized the 5-Mark coins (62.5 % Ag) representing about 870 t of fine silver.

The following table gathers all the available informations on silver recovery from coinage in the EEC countries during the recent years.

Silver recovery from coinage in the EEC countries

| | |
|---|---|
| Belgium | Silver coins generally contain 83.5 % Ag. Non silver coins are most often made of a cupro-nickel alloy (75 % Cu - 25 % Ni), or a brass alloy for the small values.<br>Past recovery programmes :<br>1968-69 20-Bf. coins representing about 250 t alloy, a large part of which was refined and sold on the market;<br>1974 50-Bf. coins re-used to mint the 250-Bf. coins commemorating the 25th. anniversary of King Baudouin's coronation;<br>1979 100-Bf. coins, demonetized in view of the disparity between face value and metal content value of the coin; will probably be re-used for the 150th. anniversary of the Belgian independence commemorative coins (250 Bf.). |
| France | Recovery programme in 1975 : 1,776 kg were melted from the demonetization of the 100-FF. coins minted by the New Hebrides condominium : 85,080 coins were recovered from the 200,000 coins in circulation.<br>Demonetization of the 5 and 10-FF. coins is to be expected because of the increasing discrepancy between the face value and the metal value of the coins : the 5-FF. coins contain 10 g Ag and there are 195.2 mln coins in circulation; the 10-FF. coins contain 18 g Ag and 39 mln coins are in circulation. |
| West Germany | Large scale recovery programme in 1976 : 871 t Ag were melted from demonetization of 5-Mark coins (62.5 % Ag), half of which was refined in West Germany, the other half was exported to and refined in Switzerland. |
| Italy | No information available. |

| | |
|---|---|
| United Kingdom | Silver coinage was demonetized in 1947, but large quantities of coins are still in the hands of private holders :<br>in 1972, 28 t of demonetized coins were recovered by the Bank of England and sold on the London market and, in 1973, 31 t were sold following the demonetization of coins withdrawn from circulation during over several years. |

Sizeable quantities of demonetized coins or silver commemoratives are capitalized in private hands and appear on the market when silver prices are booming; such a phenomenon took place in 1974, bringing the total silver coin melt to 1,462 t.

As far as the future evolution of silver supply from demonetized coins is concerned, several factors should be borne in mind :

- the recent evolution of silver prices upward discourages the use of silver in new coinage and hence lessens the potential future supply from coin melt;
- the actual size of the stock of silver-bearing coins held in private hands is impossible to determine;
- governments' intentions as to reclamation programmes are unpredictable;
- demonetization programmes do not necessarily imply immediate supply of silver on the market : part of the silver recovered from coin melt can be re-used for new coinage or its sale can be delayed according to price conditions, treasury needs, political decisions.

Considering the above, it should be expected that the global availability of silver from coin melt will gradually decrease in the long term, but yearly supply from this source will always be subject to rather large fluctuations linked to governments' decisions on demonetization programmes and price elasticity of this kind of supply source.

### 1.2.5. Silver stocks

All the informations available on silver stocks allow to distinguish between

- reported private stocks;
- government's stocks;
- conjectural stocks.

According to Handy & Harman's estimates, a total of 23,122 t Ag was held in stock in 1978, i.e. about 2 % down from the 1977 level. It should be reminded that the total world consumption in 1978 amounted to 13,157 t Ag. Table 1.2.e. details the composition of the total silver stocks in 1978.

Table 1.2.e. - 1978 Silver stocks

| Nature | mt Ag | % change with reference to 1977 |
|---|---|---|
| Reported private stocks | | |
| LME | 715 | + 19.8 |
| COMEX | 1,810 | - 15.1 |
| CBT | 1,863 | - 3.7 |
| U.S. industry stocks | 765 | - 31.5 |
| Total : | 5,153 | - 10 8 |
| Governments' stocks | | |
| U.S. GSA stockpile | 4,340 | 0.0 |
| U.S. Treasury | 1,219 | - 0.5 |
| U.S. Defense Dept. | 218 | + 4.8 |
| Other governments' stockpiles[e] | 2,488 | + 3.9 |
| Total : | 8,265 | + 1.2 |

e = estimated

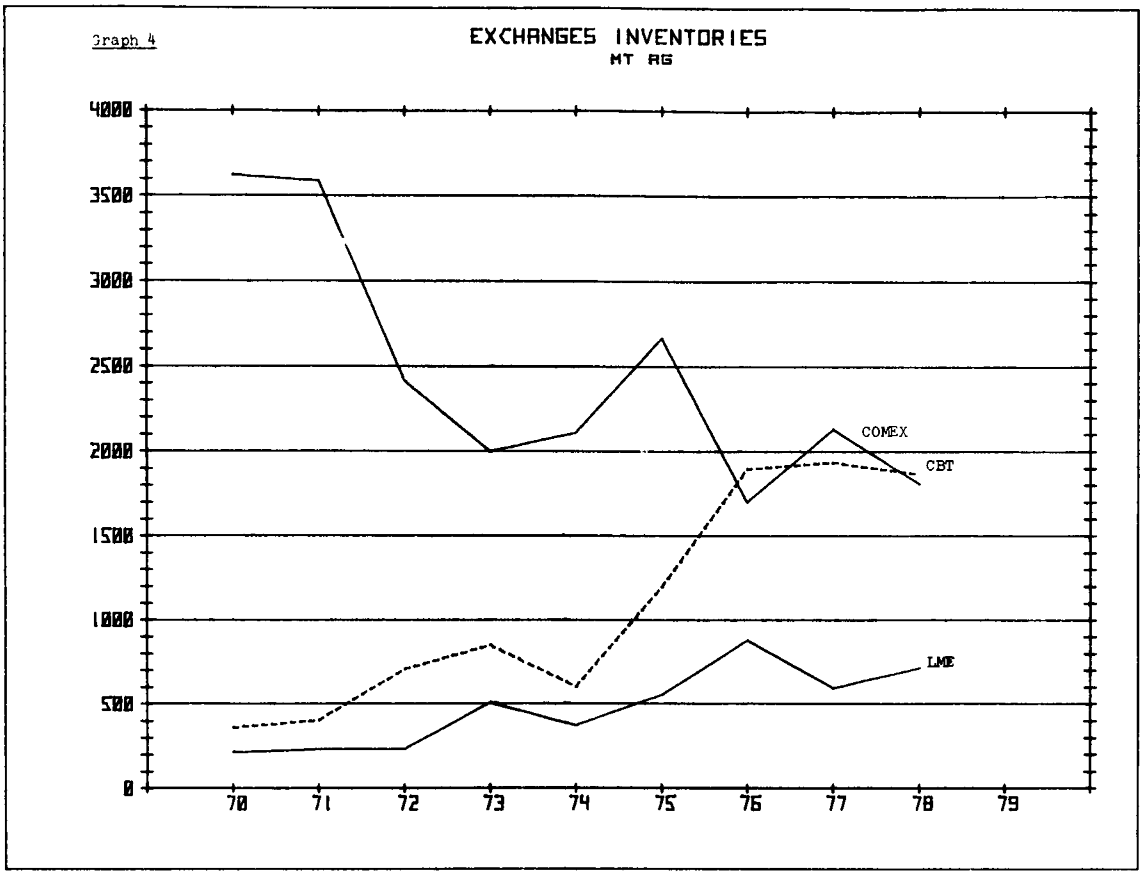
Table 1.2.e. (continued)

| Nature | mt Ag | % change with reference to 1977 |
|---|---|---|
| Conjectural stocks | | |
| Unreported industry stocks | 1,066 | + 32.0 |
| Other unreported bullion stocks | 987 | |
| U.S. silver coins potentially available | 6,718 | - 1.8 |
| Foreign silver coins potentially available | 933 | - 25.0 |
| Total : | 9,704 | + 0.6 |
| Grand total : | 23,122 | - 2.0 |

Source : Handy & Harman.

Reported private stocks refer to the stocks of the Exchanges and to the U.S. industry stocks.

Graph 4 shows the evolution of the Ag inventories on the LME, the COMEX and the Chicago Board of Trade (CBT). It should be noted that the LME and the COMEX inventory levels fluctuate in opposite directions since arbitration and hedging operations are often made from one market to the other.



Graph 4

EXCHANGES INVENTORIES
MT AG

Fluctuations in Exchanges' inventories to some extent reflect changes in private stocks, although Exchange operations do not necessarily imply physical movement of the metal and are mainly paper operations.

As far as the industry stocks are concerned, the only reporting country is the U.S.A. where industrial inventories amounted to 765 t Ag in 1978, i.e. 15 % of the consumption. The stock/consumption ratio is undoubtedly influenced by the price level, since the higher the price, the higher the financing charges and the taxation on held inventories. This ratio came down to an exceptionally low level in 1978 in the U.S.A. after having fluctuated between 18 and 28 % during the last five years. A way to estimate the industry stocks in the other countries is to generalize to those countries the stock/consumption ratio observed in the U.S.A. Following this procedure, the industry stocks of 1978 in the rest of the world are evaluated at 1,066 t Ag

Governments' stocks refer to national strategic stockpiles and to inventories piled up by national institutions. Once again, detailed information is available only in the case of the U.S.A., where government's stocks distribute as follows :

. the GSA strategic stockpile amounting to 4,340 t of Ag; this tonnage should be disposed of in the future since the present stockpile objective is zero; in this respect, the Senate Armed Services Committee voted last September the approval of a 466-t sale; however, this decision has still to receive approval by the full Senate before sales could start;

. the U.S. Defense Department inventory, mounting to 218 t by September 1978;

. the U.S. Treasury stock, mounting to 1,219 t Ag piled up partly in expectation of the Olympic coinage programme to be run in 1984 at the occasion of the Los Angeles Olympic Games.

U.S. Government's stocks totalled 5,777 t Ag at the end of 1978. Government inventory data are not systematically available for the other countries; however, it is estimated that other governments' stockpiles amounted to a total of 2,488 t Ag at the end of 1978, with 218 t in Mexico, 149 t in Japan and 90 t in France. France seems to be the only EEC country to hold a strategic stockpile.

Conjectural stocks refer to the availability of silver in the form of silver coins potentially available and to unreported bullion stocks privately held. Indian silver is not included in the conjectural stocks. The latter reached very high levels during the years preceding 1971 when the U.S. Treasury disposed of its large stocks which are now largely absorbed. The conjectural stocks were estimated to reach 8,640 t Ag in 1978, 88 % of which in the form of coins.

The present silver price and inflation are certainly strong encouragements for private investors to accumulate silver as a hedge against monetary erosion and as a high-return commodity, thus limiting the supply of silver from this source in the future.

## 1.3. EEC silver industry and supply structure

The EEC silver industry is not completely integrated since it lacks adequate domestic primary silver sources to supply the metallurgical production units. Integration, however, fully exists from the metallurgical stage up to the manufacturing stage.

Silver recovery from ores mined in the EEC was discussed in section 1.1.3. and the main components of the industry structure starting from the metallurgical stage are gathered in table 1.3.a. It is important to clearly distinguish between metallurgical producers (precious metals refining units integrated into base metals refineries) and silver refiners and fabricators who do not handle the metallurgical treatment of silver-containing minerals.

Table 1.3.a. was made out on the basis of incomplete informations and does not claim to give an exhaustive picture of the EEC silver industry.

The flows of Ag-bearing materials supplying the EEC silver industry cannot be stated precisely, partly because of the industry integration, partly because Ag-bearing materials are not necessarily recorded with reference to their silver content.

The supply to the metallurgical producers consists of Ag-bearing materials resulting from the metallurgy of base metals and of Ag-bearing scrap. The supply to the refiners and fabricators consists of Ag ingots, shots or granules, and of Ag scrap and residues.

A tentative analysis of the supply flows at the different stages of the industry gives rise to the following considerations :

a. The silver production of metallurgical producers, such as Peñarroya, Preussag, Norddeutsche Affinerie, MHO, is largely linked to their own metallurgical production of base metals which is based essentially on imported concentrates or

Table 1.3.a.

| Company | Connection | Type of activity | Remarks |
|---|---|---|---|
| **BELGIUM** | | | |
| Metallurgie Hoboken-Overpelt | Société Générale de Belgique | metallurgical producer | 1,800 t Ag/year, at Hoboken.<br>feed : - silver-bearing materials resulting from Pb, Cu and Zn metallurgy<br>- various kinds of scrap |
| Etma | - | smelter and refiner | a few tons Ag per year, at Wilsele.<br>feed : all kinds of industrial scrap |
| Johnson Matthey & Pauwels | Johnson Matthey & Co. (U.K.) | refiner and fabricator | a few tons Ag per year.<br>feed : industrial scrap<br>manufacture of industrial jewelry and dental products, mainly |
| **FRANCE** | | | |
| Peñarroya | Imetal (Rotchild group) | metallurgical producer | 1978 production : 203,529 kg Ag, at Noyelles-Godault<br>feed : silver-bearing materials resulting from the metallurgy of Pb and Zn |
| Comptoir Lyon Alemand Louyot | | refiner and fabricator | . 200 t Ag/y recovered from old scrap at Vienne<br>. ± 4500 t Agscrap/y of refining capacity at Vienne and Noisy-le-Sec<br>. fabrication of semis at Noisy-le-Sec, Villeurbanne (wire drawing), Fontenay-Frésigny (electro-mecanics) |

| Company | Connection | Type of activity | Remarks |
|---|---|---|---|
| FRANCE (continued) | | | |
| Compagnie des Métaux Précieux, and affiliates | | refiner and fabricator | . fabrication of semis at Ivry and at subsidiaries' plants : Courargent (wire drawing) and Samex (electrotechnics)<br>. scrap treatment by Meprex |
| WEST GERMANY | | | |
| Preussag A.G. Metall | Preussag A.G. | metallurgical producer | 100 t Ag/y (91.6 t Ag in 1977)<br>feed : residues from Pb-Zn metallurgy |
| Berzelius Metallhütten | Metallgesellschaft | metallurgical producer | 124 t Ag in 1977 at Binsfeldhammer from Pb-Ag residues (doré silver) |
| Norddeutsche Affinerie | Metallgesellschaft - The British Metal Corp. - Degussa | | 600 t fine silver per year at Hamburg<br>feed : Cu electrolysis slimes, Pb-Ag residues, scrap |
| Degussa | - | refiner and fabricator | 1,500 t Ag per year<br>all semis |
| W.C. Heraeus | - | refiner and fabricator | all semis |

| Company | Connection | Type of activity | Remarks |
|---|---|---|---|
| ITALY | | | |
| Pertusola | Peñarroya | metallurgical producer | 1978 production :<br>. 3.8 t fine silver<br>. 22.6 t Ag contained in Pb sulphate and Cu matte |
| Metalli Preciozi | Johnson, Matthey & Co Ltd. | refiner and fabricator | contacts, brazing alloys, dental alloys, catalysts, gauges, industrial jewelry semis, salts... |
| Ditta Gori e Zucchi | | fabricator | silversmith and jewelry products |
| NETHERLANDS | | | |
| Drijfhout & Zoon's | Comptoir Lyon Alemand | fabricator | Ag compounds; melting, rolling and drawing of Ag<br>feed : Ag bars |
| UNITED KINGDOM | | | |
| Britannia Lead | MIM Holdings | producer | 1978 production : 321,359 kg of 99 % Ag at the Northfleet refinery<br>feed : Pb-Ag residues |
| Johnson, Matthey & Co. Ltd. | | refiner and fabricator | 1,800 t Ag/year<br>can treat low Ag-containing scrap |
| Engelhard | Engelhard Minerals & Chemicals Corp. | refiner and fabricator | |

blister (in the case of Cu). Therefore, the outlook of the supply to these base metal refiners of Ag-rich copper, lead or zinc concentrates and blister is of prime importance as regards the future production rate of their precious metals refining units.

b. Some base metals refiners do not process themselves their Ag-bearing residues (Pb-Ag residues, Cu anodes slimes) and have them treated by other metallurgical producers or Ag refiners, either in the country or abroad; this practice may go along with export/import movements which are not easily balanced, since Ag gets out of the country in a base metal residue and eventually comes back to the country of origin as fine silver; a few such examples are to be found in France :

   . Compagnie Royale Asturienne des Mines can recover, since 1978, as much as 15 t/year of Ag in Pb-Ag residues resulting from the Zn metallurgy at its Auby-les-Douai plant; these residues are exported for treatment.

   . Cu anode slimes from Compagnie Générale d'Electrolyse du Palais contained 37 t Ag in 1978; these slimes are usually exported for treatment and the resulting fine silver is partly re-imported.

   . Vieille-Montagne can recover as much as 30 t Ag per year in Pb-Ag residues resulting from the Zn metallurgy at its Viviez plant. These residues are processed elsewhere.

c. In the EEC, industrial scrap is usually treated in the country where it is generated since treatment facilities of adequate capacity exist on each market and the tariff structure discourages Ag scrap import/export movements between the EEC countries (especially in France); the main non-EEC suppliers of industrial silver scrap are the U S.A., Australia and South Africa, long-distance freight costs being largely offset by the value of the Ag content of the scrap materials.

d. The large integration of the industry at the refining-manufacture level as well as the supranational structure of its major components (Johnson Matthey, Degussa, Comptoir Lyon Alemand) give rise to fine silver movements between the EEC countries which are not necessarily linked to additional processing, but are rather connected with commercial operations or input material mix requirements.

The above considerations show the quasi-impossibility to connect accurate tonnages with the various components of Ag supply to the EEC silver industry so far as it consists of

- imported and domestically produced Pb, Zn and Cu concentrates;
- imported and domestically produced blister;
- imported and domestically produced Pb-Ag residues and Cu anode slimes;
- imported and domestically produced industrial scrap.

Turning to the fine Ag supply flows, import-export statistics outline that, except for the Netherlands, all the EEC countries depend on non-EEC countries for more than 50 % of their requirements. Table 1.3.b. emphasizes that situation for 1977.

Table 1.3.b. - EEC imports of unwrought silver (°) in 1977

(mt Ag)

| | from EEC countries | from non-EEC countries | | Total |
|---|---|---|---|---|
| Belgium | 472 | 712 | 60 % | 1,184 |
| France | 660 | 716 | 52 % | 1,376 |
| Germany | 579 | 1,002 | 63 % | 1,581 |
| Italy | 290 | 485 | 63 % | 775 |
| Netherlands | 113 | 20 | 15 % | 133 |
| United Kingdom | 150 | 969 | 87 % | 1,119 |

(°) Items 71.05.010 - 71.05.030 of the Brussels' nomenclature, or items 681.11 of the SITC nomenclature.

Detailed import statistics by country of origin are presented in appendix 2 and show the importance of India, Mexico and the U.S.A. in the total non-EEC supply.

Statistics on fine silver exchanges in the EEC-countries are partly relevant only, if we consider remark (d) made above, and it should not be expected to get from them a clear picture of supply flows between the EEC countries if supply is understood to be "supply for processing". Appendix 3 details those exchanges for 1977.

# Chapter 2 - SILVER CONSUMPTION

## 2. SILVER CONSUMPTION

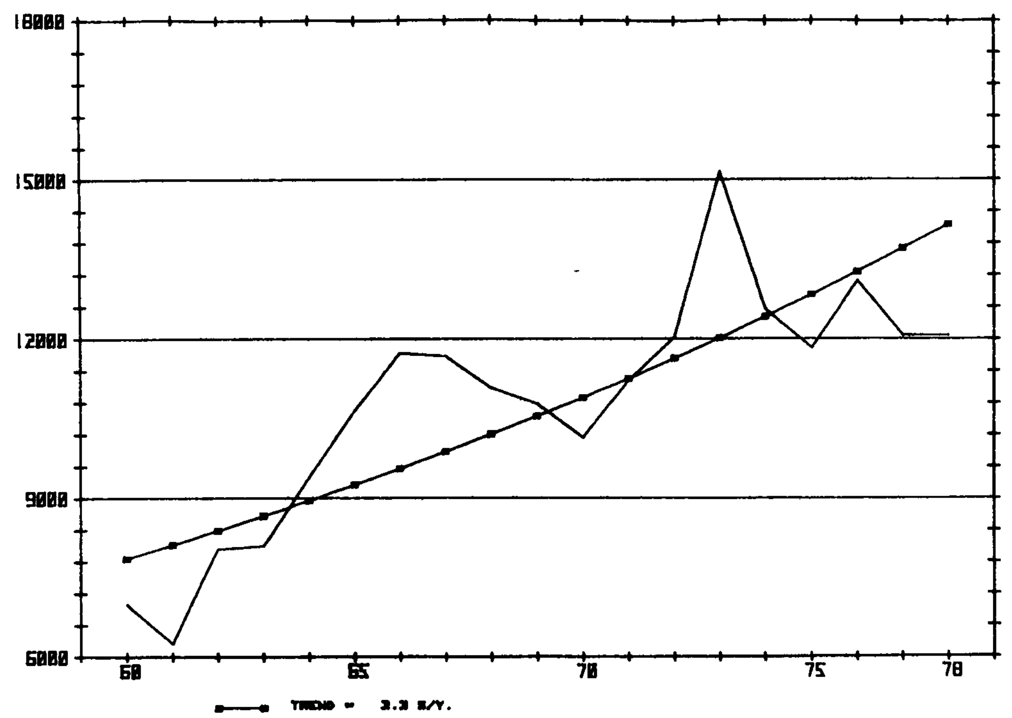
Silver consumption in the market economy countries rose to 13,157 mt in 1978, 92 % of which was used in the industry and 8 % for coinage.

The evolution and the breakdown by country of the total silver demand over the last five years are given in the following table. (mt Ag)

| Industrial uses | 1978 | 1977 | 1976 | 1975 | 1974 |
|---|---|---|---|---|---|
| USA | 4,961 | 4,777 | 5,303 | 4,905 | 5,505 |
| Japan | 2,000 | 1,950 | 1,888 | 1,443 | 1,446 |
| France | 690 | 641 | 591 | 659 | 482 |
| West Germany | 821 | 1,051 | 1,580 | 1,210 | 1,863 |
| Italy | 809 | 840 | 877 | 899 | 1,201 |
| United Kingdom | 902 | 995 | 871 | 871 | 778 |
| India | 622 | 547 | 560 | 404 | 466 |
| Other non-communist countries | 1,263 | 793 | 837 | 824 | 526 |
| Total : | 12,068 | 12,040 | 13,007 | 11,720 | 12,721 |
| Coinage | | | | | |
| USA | 3 | 12 | 40 | 84 | 31 |
| Austria | 295 | 218 | 215 | 417 | 174 |
| France | 345 | 215 | 208 | 162 | 3 |
| West Germany | 112 | 75 | 90 | 138 | 238 |
| Other non-communist countries | 323 | 187 | 109 | 87 | 109 |
| Total : | 1,089 | 715 | 924 | 1,207 | 868 |
| Grand total : | 13,157 | 12,755 | 13,931 | 12,927 | 13,589 |

Source : Handy & Harman.

As is the case for most of the base metals, the growth of silver demand from the industry has been slowing down since the early 70's: the 6.9 % per year growth rate prevailing during the 60's came down to 1.4 %/year during the 70's.



GRAPH 5 TOTAL WESTERN WORLD INDUSTRIAL SILVER CONSUMPTION
MT AG

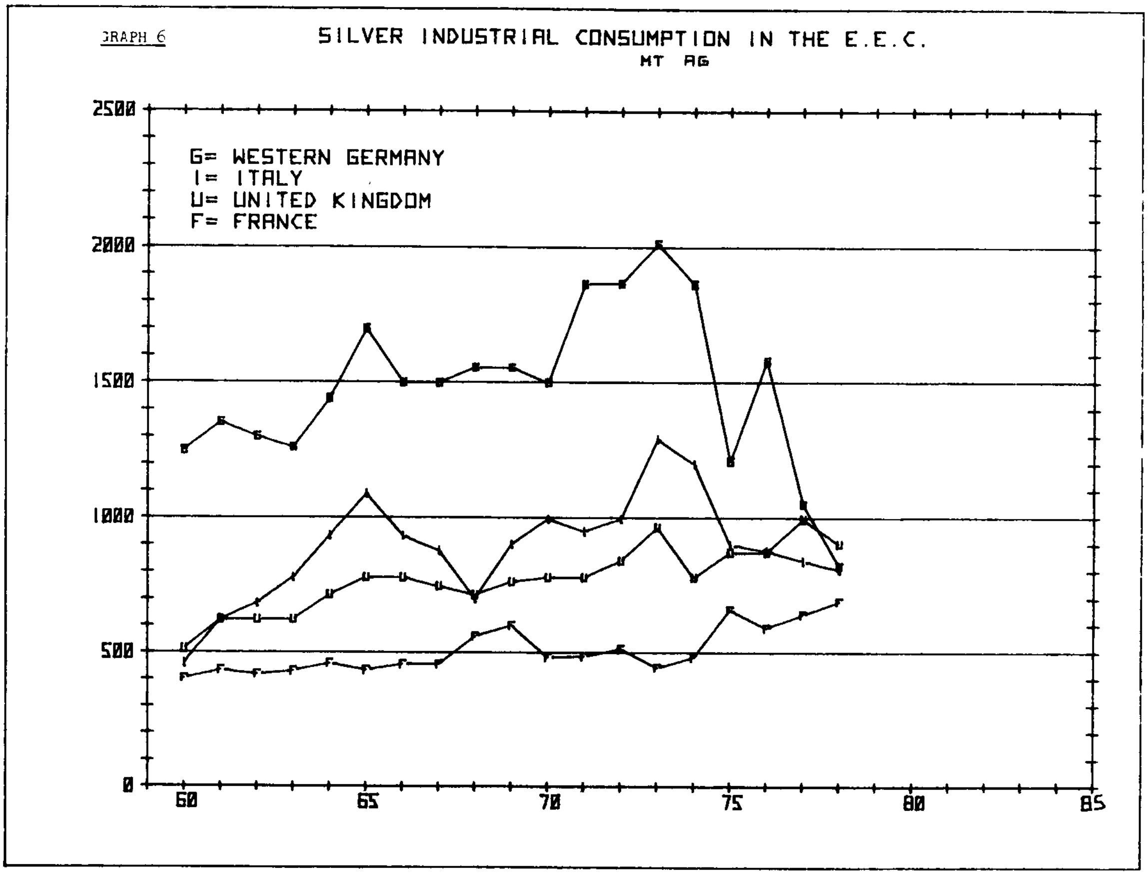
The overall growth rate over the period 1960-1978 is estimated at 3.3 % per year for the market economy countries as a group, with slight differentiations from one country to another :

| Country | % 1960-1978 growth rate |
|---|---|
| Market economy countries | 3.3 |
| USA | 3.0 |
| Japan | 8.4 |
| France | 2.4 |
| W.Germany | - 0.3 |
| Italy | 2.3 |
| U.K. | 2.6 |

The downward trend of consumption in West Germany is linked to statistical errors in the recorded consumption figures which have been overestimated for the period 1973-76 and probably underestimated for the period 1977-78. Therefore, the - 0.3 % rate should not be considered as valid.

The U.S. industry is by far the largest silver consumer of the non-communist world, it accounts for slightly more than 40 % of the industrial demand. The share of Japan is slowly increasing, rising from 13 % in the early 70's to 16 % in 1978 Industrial silver consumption in the EEC countries reached about 3,900 mt in 1978, i e 30 % of the western world consumption, with an estimated 902 mt consumed in the United Kingdom, 821 mt in Germany, 809 mt in Italy, 690 mt in France and 678 mt in the other EEC countries (essentially Belgium).

Graph 6 compares the evolution of industrial silver consumption in those EEC countries for which published data exist.


GRAPH 6 SILVER INDUSTRIAL CONSUMPTION IN THE E.E.C. MT AG

Silver demand for industrial uses generally follows the fluctuations of the business cycle, the photography and the elec-electronic industries being the major end-user sectors. Brazing alloys, jewelry and silverware absorb non-negligible quantities of Ag whilst the requirements for minor uses such as catalysts, mirrors, dental and medical supplies are much smaller.

Silver consumption for industrial uses in the EEC countries compares as follows with the distribution prevailing in the USA and Japan (% of 1978 total consumption excluding coins, medallions, commemoratives) :

| End-uses | EEC | USA | Japan |
|---|---|---|---|
| photographic materials | 41 | 38 | 50 |
| electrical/electronic products | 15 | 24 | 23 |
| brazing alloys and solders | 13 | 7 | 7 |
| jewelry and silverware | 20 | 22 | 3 |
| miscellaneous (mirrors, dental and medical supplies, catalysts...) | 11 | 9 | 17 |

The relative development of the various consuming sectors in each country justifies the differences in silver consumption breakdown.

More than one third of the silver needs during the early 60's arose from the use of silver for coinage, which now appears as a minor use representing 6 to 8 % only of the total demand. This structural change in the total silver consumption occurred during the last decade and is discussed under section 2.6.

The following sections review the industrial uses of silver with specific reference to the situation prevailing in the EEC countries.

## 2.1. Photography

### 2.1.1. The usage of silver in the photography industry

The photography industry uses silver in the form of its halogen compounds deriving from silver nitrate ($AgNO_3$). The silver nitrate is produced from commercial (99.9 %) or refined (99.99 %) silver, either at the user's plant or at the Ag refineries (such as Johnson Matthey Chemicals or Comptoir Lyon Alemand in Europe).

It is important to note that the photography industry is well organized to recycle as much Ag as possible, either during or at the end of the manufacturing processs (fabrication losses, flaws, waste waters...) and, in a lesser proportion, after the end-products have been used (reclaimed films, radiographies, developers,.. ). It is however impossible to specify what share of the total silver needs of the industry is satisfied by recycled Ag, in view of the fact that :

- the source (primary or secondary) of the raw materials serving as feed at the initial stage of production is not detectable;
- the photo producers are reluctant to disclose the percentage of silver arising from in-house recycling as it could give an idea of the extent of their process efficiency, such percentage being also a function of their product mix.

The halogen compounds of silver ensure the light sensitivity of films, photo paper and cloth : films are dipped in a mixture containing silver salts and the sensitive surface is impregnated with a very thin film of precious metal. The image definition obtained through the use of silver salts is unsurpassed for clarity, since Ag-treated sensitive surfaces are ten times as sensitive to light as competitive silverless products.

Specific applications (radiography, colour photography, microfilming, graphic arts, ...) govern the Ag specification requirements, the techniques used, the quantities consumed and the recovery rate after use :

| Application / product | Average Ag content g/m2 | Average Ag content (as % of product weight) | Average Ag content after use (as % of product weight) | Nature of support | |
|---|---|---|---|---|---|
| | | | | Polyester | Cellulose triacetate |
| - Medical radiography | 10 | ( 2.5 - 3.5 | 1.2 - 1.35 | x | |
| - Industrial radiography | 20 | ( | 1.2 - 1.35 | x | |
| - Photographic paper | 8 to 9 | 0.5 - 0.7 | 0.5 | | |
| - Graphic arts | 5 | < 2.5 | < 1.2 | x | |
| - Microfilms | 2 | | | | |
| - Non-professional films | | | | | |
| black and white | 5 | 1.5 | few°/oo | | x |
| colour | 10 | 1.5 | 0 | | x |
| - Non-professional paper | | | | | |
| black and white | 1 | | | | |
| colour | 10 | | 0 | | |
| - Non-professional motion picture films | | | | | |
| black and white | | | | | |
| colour | 8 to 10 | | 0 | | |
| - Professional motion picture films | | | | | |
| black and white positives | 2.5 | 1.5 | few°/oo | x | x |
| colour positives | 2.5 | 1.5 | 0 | x | x |
| black and white negatives | 7.5 | | few°/oo | x | x |
| colour negatives | 7.5 | | 0 | x | x |

Source : Kodak Pathé.

The difference between the Ag content of the various products before and after use is due to the fact that some Ag is lost in the developing baths. The specific consumption by use may vary within a ± 20 % range around the figures mentioned in the above table since each producer develops original features in the manufacturing technology and for each product there are several different specifications.

Technological progress is generally the result of : lesser use of silver thanks to a more efficient utilization of silver, replacement by silverless photosensitive materials or development of new processes not requiring silver. As far as substitution is concerned, all the photo products do not offer substitution opportunities : in instant photography for example, no other materials can serve as a substitute for silver halogen compounds because their lower light sensitivity would require a longer exposure time; however, in reprography, the exposure may be increased and, therefore, less sensitive materials such as photopolymers and diazoïc products can be used, allowing significant price reductions of the final product.

Turning to silverless processes, new developments are taking place in instant reprography : scanners, magnetoscopes, video cameras, magnetic tapes sensible to electrons (substituting for radiographs), but the high total cost of these new devices still limits the generalization of their use.

Due to the diversity of the products and to the processing differences from one producer to another, it is rather difficult to specify the share of silver in the total production costs of the photography industry. Silver is estimated to represent 4 % of the total input material costs of Kodak, but it should be reminded that Kodak has a widely diversified production including chemicals as well as photo products. As for Gevaert, which is highly specialized in the photo industry and not diversified at all, it estimates the silver share in the total costs at 8 to 10 %, reaching 25 % for some products such as X-ray films.

### 2.1.2. The structure of silver consumption in the EEC photography industry

Table 2.1.a. gives the country by country breakdown of Ag consumption in the photography industry, reference to 1978.

Table 2.1.a. - 1978 Silver consumption in the photography industry

| Country | mt Ag | % of the country's industrial consumption |
|---|---|---|
| USA | 1,866 | 38 |
| Japan | 1,020 | 50 |
| EEC | 1,588 | 41 |
| Belgium | 558 | 90 |
| France | 248 | 36 |
| West Germany | 213 | 26 |
| Italy | 162 | 20 |
| United Kingdom | 407 | 45 |

The photography industry is the largest Ag consuming sector in the USA and Japan, as well as in the EEC. Its silver requirements have been growing over the period 1972-78 at an average annual rate of 5.6 % in the USA and 7.1 % in Japan; a similar growth rate cannot be mentioned for the EEC countries due to a lack of statistics.

The breakdown of Ag consumption in the EEC countries for use in the photography industry emphasizes the structure of the industry which is basically organized around a few multinational producers and their subsidiaries :

| Parent company | EEC production unit<br>Company | <br>Country | Estimates of Ag consumption |
|---|---|---|---|
| Eastman Kodak, USA | Kodak Ltd. | United Kingdom | 260 t/y |
| | Kodak Pathé | France | 240 t/y |
| | Kodak A.G.* | West Germany | - |
| Ciba Geigy, Switzerland | Ilford Ltd. | United Kingdom | 150 t/y |
| | Ilford GmbH | West Germany | - |
| | Lumière | France | 25 t/y |
| Photo Produits Gevaert, Belgium | Agfa Gevaert | Belgium | 500 t/y |
| | Agfa Gevaert | West Germany | 150 t/y |
| | Agfa Gevaert | France | 50 t/y |
| 3M, USA | 3M Ferrania | Italy | 160 t/y |

(*) Sales subsidiary not involved in production.

As far as the supply of silver to the film producers is concerned, it seems that the common practice is to buy fine silver and to have it treated into $AgNO_3$ by the silver refiners. Gevaert does, however, process the metal in its own installations, in order to ensure the high quality of its input materials.

As a rule, the film producers do not hold inventories because of the heavy financial charge it involves.

The relative importance of each EEC country in the total silver demand for the photography industry is directly linked to the geographical organization of the production within each group company. For instance, Gevaert manufactures all the professional products in Belgium, the non-professional products in Germany, and it has a smaller but largely diversified production in France. This production structure accounts for the differences in the Ag tonnages consumed by Gevaert in each country.

In this respect, changes in the production organization of those multinational companies should have an immediate impact on the Ag consumption breakdown between the EEC countries : hence, it should be expected that by 1982 the French consumption will increase to the prejudice of the British consumption, since Kodak Pathé will centre on the production of high silver content emulsions (radiography films, ...) while Kodak Ltd. will centre on colour and graphic arts products.

Moreover, the geographical spreading of companies' production may also give rise to exchange flows of input materials as well as of finished products. As an example :

- Kodak Ltd. (U.K.) sends its new scrap generated during the manufacturing process, partly to Kodak Pathé (France), partly to Eastman Kodak (Rochester, USA), for recycling;
- Kodak Pathé sends films to Kodak A.G. for sale in West Germany and supplies directly the other continental EEC countries and the former French colonies, while Kodak Ltd. supplies the free trade area and former Commonwealth countries.

Table 2.1.b. analyzes the Ag consumption in the EEC photography industry by type of application with reference to 1977.

Table 2.1.b. - Sensitive surfaces production in the EEC by type of application

| | Million US$ | % of total |
|---|---|---|
| Non-professional and professional films (black and white and colour) | 630 | 30 |
| Professional cinema films | 132 | 6 |
| X-Ray films (medical and industrial) | 320 | 16 |
| Graphic arts films | 352 | 17 |
| Black and white paper | 268 | 13 |
| Colour paper | 256 | 12 |
| Paper for reproduction | 116 | 6 |
| | 2,074 | 100 |

The value of the various types of production is based on dealer prices without taxes, and includes packing costs which may reach significant amounts according to the type of product (mainly in the case of non-professional films). Expressed in tonnage, medical radiography absorbs about half the silver consumed in the photography sector in Europe.

## 2.2. Electric and electronic industries

### 2.2.1. The usage of silver in the electric-electronic industries

Silver is used in electric-electronic applications because of its high electrical conductivity, high resistance to oxidization, low contact resistivity and high thermic conductivity.

Contact materials and electronic components represent about 85 % of the electric-electronic silver-bearing products and the batteries absorb the remaining 15 %.

#### 2.2.1.1. Contact materials

In contact materials, silver is used either as fine silver or, more often, alloyed with one or two other metals, the specific properties of which are needed to compensate for the poor mechanical properties of silver, its low melting point and its tendency to form surface films mainly by sulfuration. The silver alloys usually used in contact materials are Ag-Cu, Ag-W, Ag-Ni, Ag-Pd, Ag-Pt, Ag-graphite and also three-component alloys such as Cu-Ag-Au or Pt-Ag-Au (Cfr. appendix 2.A.).

Silver, or its alloys, is either plated or cast into massive shape.

There are three categories of applications where the use of silver as contact material is required :

a. contactors (50 %), for the electric drive of engines, for instance, Ag is then alloyed to Ni or Cd (Ag-CdO with 10 to 15 % CdO);

b. low voltage current interrupter (25 %), which must withstand soldering and, thus, incorporate refractory materials such as graphite, tungsten or tungsten carbide;

c. relays (25 %), generally used in telephony or incorporated in small electrical devices ($\leqslant$ 10A current); a large variety of contact materials are used in relays, ranging from pure Ag to alloyed Ag, principally in order to avoid corrosion and surface film formation, both of which are detrimental factors to low contact resistivity.

Finally, it must be reminded that Ag is a minor though critical component of most of the electrical appliances since it is used as a contact metal in switches.

Silver-base electrical contact materials used by fabricators of relays, switches, circuit breakers, contactors... are generally manufactured by silver refiners such as Engelhard, Johnson Matthey, Degussa, Comptoir Lyon Alemand.

The share of silver in the cost price of contact semis is generally of 50 % but it may reach 70-80 % in the low voltage contacts. It is much lower in relays and switches : 0.25 %, plastics having an approximate 20 % share in the cost price of those items.

Due to its outstanding electrical and thermal conductivity, silver can hardly be replaced in contact applications. However, mention should be made of the research programme conducted by Comptoir Lyon Alemand in France, in connection with a new Cu-Ni-Sn alloy, the properties of which could be equal if not superior (in protected atmosphere) to the properties of silver in the light-duty contacts. In another respect, technological progresses already allowed substantial Ag economies which, however, do not necessarily result in a lower price of the final product if the new "low-Ag-consuming" process itself is more expensive. In this respect, the evolution that occurred in riveting processes are striking :

- rivets were initially cast in pure or alloyed silver, such massive Ag rivets were progressively replaced by bi- or tri-metallic rivets the main body of which was made of copper or of aluminium and copper, on which a thin layer of silver was plated; finally, with the development of the powder metallurgy, the rivet itself disappeared and was replaced by a massive Ag or bi-metallic button soldered to the blade; if the latter technology is used, a 70 % reduction in Ag consumption may be achieved but, on the other hand, it implies a significant increase in the manufacturing cost; such technology may therefore only be used for new fabrications.

#### 2.2.1.2. Electronic components

Silver is used in electronic components primarily for its high electrical conductivity and low contact resistivity. The most common applications are :

- resistance components made of Ag and Pd;
- colloidal silver solutions for tantalum capacitors;
- switches and circuit-breakers;
- active components such as diodes, transistors, integrated circuits.

For these applications, gold and palladium are the main competitors of silver, not as far as price is concerned, but on the basis of performance requirements. Technological developments in the field of miniaturization and solid-state technology will have a moderating influence on the use of Ag in electronic components since new technologies avoid mechanical contacts and use platinum and palladium as preferred materials.

### 2.2.1.3. Batteries

The use of silver in the battery industry is rather recent, though it was already being experimented in the early days of electrochemistry. Generally, when compared with other battery systems, the major advantage offered by each of the silver battery systems available to-day, is high energy output per unit weight and space. The major disadvantages of silver systems are relatively short life and higher cost, which are serious handicaps for most of the commercial applications. Therefore, about 90 % of the silver battery market is concerned with defence and space applications where requirements are rigorous and price considerations not vital.

Ag-containing batteries break down into five categories :

#### (a) the silver oxide-zinc secondary batteries

They are being used in applications where energy produced per unit of weight and space are of prime importance and where their relatively high cost and short life are acceptable, i.e. mainly military and space applications, such as torpedoes, missiles, manpack radios, aircraft, submarines, sounding balloons, satellites and space vehicles... If the life of the silver oxide-zinc secondary battery could be increased to six years, instead of two, many commercial applications would become feasible.

The labour costs related to the manufacture of those batteries are currently very high because automation cannot be introduced in the production process in view of the small volume of those batteries.

#### (b) the silver-oxide-zinc primary batteries

They are used when ability to produce instantaneously full wattage and capacity is required (ex. torpedoes); these batteries have excellent shelf life prior to activation and, if stored at reasonable temperatures (below 40°C), very little change in battery characteristics will occur over a five-year period.

(c) the silver oxide-cadmium batteries

They are used when the application requirements call for a compromise between the short life - high energy density of the silver-zinc system and the long life - low energy density of the nickel-cadmium system (torpedoes and aircraft, satellite, ...).

(d) the silver chloride-magnesium batteries

These primary batteries are activated upon use by immersion in sea-water or fresh water which serves as the electrolyte. They find their main applications in military uses, chiefly as power producer for torpedoes and sono buoys.

(e) the button cells

Very small button-shaped, non-reserve type silver oxide-zinc primary celles have been developed for power hearing aids, electric watches and thin calculators. The capsule of those batteries contains, on the average, 85 % $Ag_2O$, 10 % $MnO_2$, 5 % C. They show a low and consistent internal impedance. Their low temperature performance is good when compared with existing batteries. They have an excellent retention capacity after storage and will deliver 90 % after one year of storage at 20°C.

The input materials for the manufacture of batteries are either silver oxide (for button cells) or silver nitrate, unfold threads, bars, silver chloride (for military use batteries). Those silver products are usually produced at the silver refineries.

The share of silver in the total manufacturing costs of a battery may vary from 50 % in the case of button celles, to 15 % in military use batteries. Recycling of the latter is well organized and allows to disregard the silver price as a detrimental factor to their use. Higher efficiency in the recycling of button cells is developing, mainly through the intermediary of the end-product fabricators themselves (manufacturers of watches, auditive devices, microcalculators,...)

Silver oxide has not many substitutes in the high-performance applications for which it is in great demand, i.e. in military applications and in all the applications where miniaturization requires very small batteries.
Mercury oxide could replace silver oxide in button cells, but such substitution is restricted in view of the pollution problems arising from the use of mercury. Manganese oxide and lithium are possible substitutes in some cases, especially in button cells used to produce LDC devices. In re-chargeable minicalculators, zinc oxide is preferred to silver oxide. Beside some new applications such as thermal propulsion in Europe, no exceptional development is expected in the military sector where the new oxygen-hydrogen type of batteries could develop and meet new market requirements in place of silver oxide batteries.

### 2.2.2. The structure of silver consumption in the EEC electric-electronic industry

The elec-electronic industry is the second largest silver consuming sector, after photography, in most of the industrialized countries. Table 2.2.a. shows the breakdown of the silver demand from this sector by country, with reference to 1978; EEC figures are largely based on estimates and the Japanese consumption covers the Ag used for contacts and for plating.

The United Kingdom, France, Italy and West Germany are significant users of silver in contacts and conductors which are by far the chiefest silver consuming applications in the elec-electronic industry. The silver materials used for the manufacture of those products are usually produced by the big silver refiners, i.e. Johnson Matthey, Comptoir Lyon Alemand, Degussa, and their affiliates, which offer not only the base materials but also a range of semis.

Table 2.2.a. - 1978 consumption of silver by the elec-electronic industry

| | Total consumption in elec-electronic industry | | Contacts & conductors | | Batteries | |
|---|---|---|---|---|---|---|
| | mt Ag | % of total country consumption | mt Ag | % of total | mt Ag | % of total |
| USA | 1,173 | 24 | 980 | 20 | 193 | 4 |
| Japan | 468 | 23 | 215 | 11 | n.a. | |
| EEC | 587 | 15 | | | | |
| Belgium | 6 | 1 | | | - | - |
| France | 138 | 20 | 123 | 18 | 15 | 2 |
| W.Germany | 131 | 16 | n.a. | | n.a. | |
| Italy | 105 | 13 | 105 | 13 | - | - |
| U.K. | 207 | 23 | 107 | 19 | 40 | 4 |

The most important end-users in the sector are :

- in France :
  Télémécanique, Merlin Gérin, Samec ...
- in West Germany :
  Siemens
- in Italy :
  Siemens Elettra, NCR, Télémécanique, ...
- in the United Kingdom :
  Sheffield Smelting, GEC (Elmet Alloys), Plessey, STC (ITT).

Competition is very strong in that market and research is conducted mainly at the Ag refineries. Research laboratories of the electric industry, such as LCIE[*] in France and ERA[*] in the United Kingdom, are also currently involved in research programmes for the end users, in cooperation with the refiners.

[*] LCIE : Laboratoire Central des Industries Electriques et Electroniques.

ERA : Electrical Research Association.

As far as the electronic components are concerned, they are manufactured either by subsidiaries of large international groups such as RTC Compelec, a Philips' subsidiary in France, or LTT, an affiliate of ITT, or by small companies who specialize in those products and are much more numerous. The total quantities of silver used in the EEC countries for electronic components represent less than 1 % of the total EEC silver consumption, but this type of demand benefits from the strong growth of the electronic industry (i.e. around 10 % per year).

The EEC battery industry produces essentially military batteries and button cells. The United Kingdom and France are the European leaders; they consumed 40 and 15 tons of silver respectively for battery production in 1978. Table 2.2.b. describes the structure of the battery industry in the U.K., France and West Germany. It results from the establishment of large battery producing companies on the consumer markets and from the development by the user of its own production lines (by Timex for instance, who is basically a watch producer).

Table 2.2.b. - Battery producers in the EEC

| | United Kingdom | France | West Germany |
|---|---|---|---|
| Batteries for military uses | SOGEA Batteries (CGE)<br>Chloride Industrial Batteries<br>Mallory | SOGEA (Compagnie Générale d'Electricité)<br>Wonder | Silberkraft |
| Button cells | Timex<br>Berec Micro batteries (Ever Ready/Union Carbide)<br>Mallory<br>Varta | Leclanché (SAFT) | Varta A.G. |

Strong competition, especially in button cells, is experienced from the Far Eastern producers, principally from Japan. Product development and research work are generally conducted by the battery producers themselves, as it implies highly sophisticated and long lasting testing procedures.

## 2.3. Brazing alloys and soldering

### 2.3.1. The usage of silver in brazing and soldering

The role of silver is fundamental in brazing : it improves the properties of base metals alloys used for brazing, it increases their corrosion resistance and tensile strength and gives them higher electrical conductivity.

Silver-bearing brazing alloys have the ability to wet the base metals at temperatures below their melting point. Such alloys do not dissolve or attack steel in normal use, their ductility prevents the bending of joints, they retain strength at a wide range of temperatures and join a variety of materials.

The base metals composing the silver-bearing brazing alloys are Cu, Zn, Sn or Cd. Silver is added in variable proportions, which may be as high as 50 % in some applications. Safety regulations and pollution concern are in some respect favouring the use of silver in brazing alloys; for instance, they led to the replacement by silver of part or all of the cadmium contained in some brazing alloys in order to increase their melting point; in this respect, Johnson Matthey developed a new alloy for central heating applications, the characteristics of which (55 % Ag - 45 % Zn - mp 630-650°C) favourably compare to that of the common leading alloy (42 % Ag - 43 % Zn - 15 % Cd - mp 608-617°C).

Another example is the expanding use of tin-silver solder in tube plumbing instead of tin-lead solder. Tin-silver solder consists of 96.5 % Sn and 3.5 % Ag (melting point 221°C) It is easy to apply, it provides high strength to finished joints and does not contain polluting elements such as Pb which is a great advantage when used in applications where joints come into contact with items intended for human consumption, such as drinking water. The cost differential is insignificant because less of that new solder is required and less labour is needed for its application.

However, for some time, the silver content of the brazing alloys has been showing a tendency to decrease with maxima dropping from 50-60 % to 42 % and minima moving from 30-40 % to 20-38 %. Furthermore, phosphorus brazing is competing successfully with silver brazing in some applications and automation of the brazing operations can lead to lesser use of silver as a consequence of higher efficiency in brazing and use of lower silver-containing brazing materials (brazing paste).

Brazing alloys are generally supplied by the manufacturers of semis, i e. the Ag refiners; they are offered in various shapes : wires, rods or preformed. The latter shape is gaining importance because, the brazing alloy being cast to the shape of the element to be brazed, losses during brazing are much reduced.

The main brazing applications requiring silver-bearing alloys are developing in :

- the automobile industry; for instance, a Renault car requires 10 to 20 g Ag for its forepart;
- railway and sea transport;
- the mechanical industry, mainly machine tools;
- the aeronautic and aerospace industry, where the use of silver is essential because the reliability of brazing points is vital, brazing is applied very carefully and subject to tight

controls, starting at the level of the impurity rate of the brazing alloy used;

- the consumer goods industry (refrigerators, washing machines...)
- the housing industry (sanitary ware, gas pipes, refrigeration and air-conditioning apparatuses

The share of brazing, and thus of silver, in the cost price of the finished products is very low and often less than 1 %.

### 2.3.2. EEC consumption of silver in brazing alloys

Silver brazing is apparently a more widespread practice in Europe than in the USA and Japan, as appears from table 2.3.a.

Table 2.3.a. - 1978 silver consumption in brazing alloys

| | mt Ag | % of country's total consumption |
|---|---|---|
| USA | 342 | 6.9 |
| Japan | 139 | 6.7 |
| EEC | 496 | 13.0 |
| Belgium | 25 | 4.0 |
| France | 117 | 17.0 |
| West Germany | 90 | 11.0 |
| Italy | 129 | 16.0 |
| United Kingdom | 135 | 15.0 |

The relative importance of each EEC country in the total silver consumption for brazing alloys is connected to the specific development of the end-user sectors in each of these countries, and also to the brazing technology chosen by the users (for instance, Citroën and Peugeot do not use silver brazing, whilst Renault and Talbot do use it).

The EEC needs in silver brazing alloys are not entirely met by the domestic production which is to be complemented by imports. The silver refiners (Johnson Matthey, Degussa, Comptoir Lyon Alemand) are the major suppliers, and also specialized brazing alloy manufacturers such as Castolini Italiana and W.W.Welding in Italy or Bouteiller et Bondeville, Polysoude, Sarazin and Soudure Autogène Française in France. Silver brazing alloy production in France consumes less than 10 t Ag per year and the domestic needs are largely supplied through imports ( notably from West Germany).

## 2.4. Jewelry and silverware

The intrinsic value of silver justifies the interest shown for jewerly, silverware and silver plated products. Silverware and silver plate create the bulk of silver consumption in that sector

Silver is then used in the form of an alloy called "sterling"; in the United Kingdom, the sterling alloy contains 92.5 % Ag and 7.5 % Cu, while in France the silver content reaches 95 % (the highest in the world), copper enters the alloy to improve silver hardness.

Stainless steel is a strong competitor to silver in silver plate applications, but tradition and the prestige of silver, especially in Europe, are a deterrent to extensive substitution of stainless steel for silver.

Table 2.4.a. shows the importance of jewelry and silverware in the total EEC consumption of silver. It should be noted that, in Italy, jewelry generates the largest part of consumption in this sector, while in Germany silverware is dominant.

Table 2.4.a. - 1978 silver consumption in jewelry and silverware

| | mt Ag | % of country's total consumption |
|---|---|---|
| USA | 1,048 | 21 |
| Japan | 69 | 3 |
| EEC | 800 | 20 |
| France | 180 | 26 |
| West Germany | 205 | 25 |
| Italy | 388 | 48 |
| United Kingdom (*) | 27 | 3 |

In each country, consumption is shared out by a very large number of small jewellers and craftsmen, beside a few large goldsmiths such as Christofle and Ercuis in France.

## 2.5. The other industrial uses

Silver is used is much smaller quantities in several other applications, mainly :

a. mirrors

Silver has the highest reflective potential when compared with other metals (97 % against 90-95 % for copper, gold, aluminium and 60-55 % for iron, tin and mercury); the reflectivity of the mirror results from the thin film of metal which covers the glass. In the past, silver replaced tin and now has to stand strong competition from aluminium, particularly for mirrors of large diffusion. However, Al substitution for Ag is made at the expense of long-term quality of the product since Al mirrors tarnish much more quickly than Ag mirrors.

Silver consumption in mirrors will probably benefit from the development of solar energy systems, because of the important surfaces of solar mirrors they require. For

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(*) 1979 consumption is estimated at 66 mt Ag.

instance, the experimental tower and mirror system selected by the Energy Research & Development Administration of the USA, is a 10 mW unit, the mirrors of which require about 45 kg Ag. The ERDA estimates that the construction of solar/thermal units by the year 2000 could total 1000 to 20,000 MW which would mean a silver consumption of 4,500 to 90,000 kg.

b. catalysts in organic chemistry

The use of silver in catalysts represents a few % only of the total industrial consumption of silver; the Ag input material may widely vary according to the specific application.
For instance :

| | | |
|---|---|---|
| - pure Ag bars or needles silver nitrate | for | oxidization of methanol in formaldehyde |
| - porous silver powder | | ceramic balls |
| - silver sulfocyanate | | ethylene oxidization in ethylene oxide |
| - silver sulfate | | sulphuric anhydride |
| - silver nitrate | | polymerization |

The petrochemical industry is the largest consumer of silver for catalysts. This accounts for the close relationship between silver demand from that sector and the fluctuations of the petrochemical products market.
The petrochemical industry usually buys silver as a salt or as wrought metal, and manufactures the desired compounds for catalysis application. Manufacturing processes and research work are jealously kept secret by each company of the sector.

c. pharmaceutical products

Silver can be used in disinfectant preparations and other pharmaceutical products, but its use is decreasing mainly as a consequence of new types of medicine.

d. dental and medical supplies, photosensitive glasses, antistatic carpets, meteorology and climatic control devices.

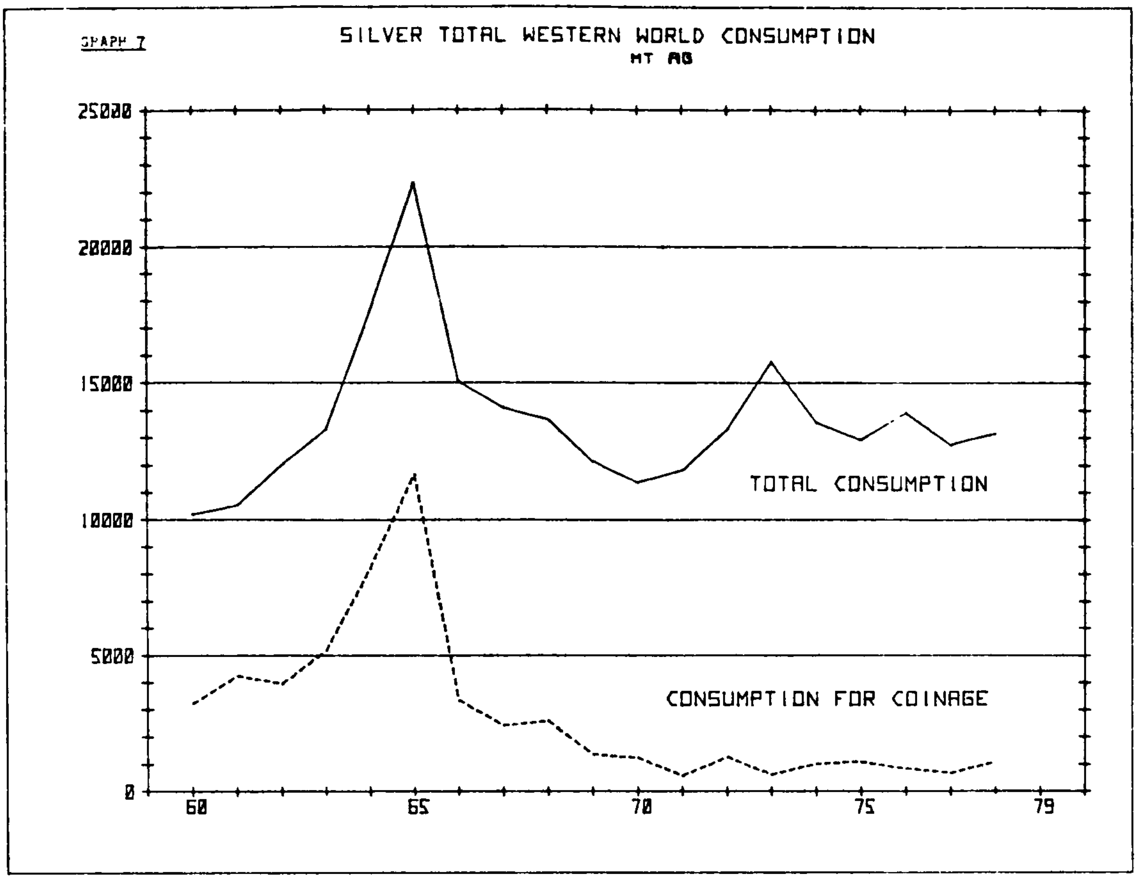
The total quantity of silver consumed for above-mentioned applications varies from one country to another according to the relative development of the consuming sector in each country. Table 2.5.a. shows an estimate of the 1978 consumption of silver in minor applications.

Table 2.5.a. - 1978 silver consumption in "other uses"

| | mt Ag | % of country's total consumption |
|---|---|---|
| USA | 529 | 10.6 |
| Japan | 140 | 6.7 |
| EEC | 429 | 11.0 |
| Belgium | 30 | 5.0 |
| France | 7 | 1.0 |
| West Germany | 181 | 22.0 |
| Italy | 24 | 3.0 |
| United Kingdom | 126 | 14.0 |

## 2.6. Silver in coinage

Coinage used to be one of the major sectors of silver use, if not the major one in some years : it represented more than 30 % of the total silver demand in the early 60's, but this share came progressively down to less than 10 % in the late 70's. Graph 7 shows the evolution of silver demand for coinage in the Western world and its relative importance as regards total silver consumption.



The 1965 peak figures relate to a large minting programme in the USA. From that time onwards, coinage silver consumption came steadily down, with occasional peaks corresponding to particular minting programmes. The major reason for the decrease of silver use in coinage is the joint effect of higher silver metal price and currencies depreciation which made silver coinage uneconomical for one or both reasons. Some countries, like Italy and Japan, completely stopped using silver for minting purposes. Some others still use it for commemorative coins only, for instance :

- 965 t Ag were used in Canada over the period 1974-76 for the Olympic Games coins;
- in the United Kingdom, undisclosed, though significant, quantities of Ag were used for the minting of the Silver Jubilee commemoratives in 1977.

In the EEC, France and West Germany still consume important quantities of Ag for coinage, amounting to 42 % of the Western world total in 1977 and 1978.

Table 2.6.a. - Silver consumption for coinage

(mt Ag)

| | World total | France | West Germany |
|---|---|---|---|
| 1970 | 1,232 | 108 | 227 |
| 1971 | 591 | 11 | 597 |
| 1972 | 1,260 | 20 | 703 |
| 1973 | 622 | 3 | 295 |
| 1974 | 1,026 | 12 | 274 |
| 1975 | 1,089 | 163 | 134 |
| 1976 | 840 | 208 | 90 |
| 1977 | 684 | 212 | 75 |
| 1978 | 1,088 | 345 | 112 |

As emphasized in table 2.6.a., silver consumption for coinage largely fluctuates from one year to another, according to minting programmes. These programmes are set up for many different reasons :

. to help reduce domestic inflation by offering a means of saving to small investors and thus reduce the money supply;
. to earn foreign currencies through the sale of medallions and commemoratives on foreign markets;
. to promote tourism;
. to induce upward pressure on the market price of the metal by reducing the availability of silver to industrial consumers.

In 1978, France and Austria were the leading consumers of silver for coinage purposes, absorbing 345 and 295 tons respectively of fine metal. Both countries pursue a similar policy which aims at reducing domestic inflation, since the newly issued silver coins are mainly distributed to old pensioners and are not circulating. French silver coins currently minted are 50-FF coins containing 90 % Ag - 10 % Cu and weighing 30 g; 12 million coins of this kind are still to be issued in 1979 (which means a silver consumption of 324 tons) in order to complete the minting programme of the 50-FF coins which started in 1974.

Mexico consumed 198 t Ag in 1978 for coinage. Banco de Mexico buys silver from Industria Peñoles and conducts a very active programme aiming at braking inflation, backing the home currency and earning foreign moneys. Until the end of 1978, it issued 100-peso coins but they became uneconomical to produce, their face value being far lower than their metal value at current prices. It is currently issuing the "onza", a non-legal tender bullion coin containing one oz of silver and selling at a 9-10 % premium over the daily London silver price fixation.

The Soviet Union is currently minting the 1980 Olympic Games coins; it consumed around 100 t Ag in 1978 for that purpose (5 and 10-rouble coins containing 99 % Ag and weighing 16.67 and 33.3 g respectively).

West Germany also consumed about 100 t Ag in 1978. This consumption relates to quarterly campaigns regularly conducted since the massive demonetization of the 5-mark coins in 1976. The coins issued are commemoratives with legal tender, their face value is 5 mark and their silver content 62.5 % (the balance is copper).

Two countries are now entering the silver coin market : Peru and China. Peru is appearing in 1979 with more than 300 t silver coins. The Central Bank's aim is to back the domestic currency and to push the silver price through buying large quantities of silver from Centromin, the state mining and marketing company. China issued silver medallions to mark the Chinese painting exhibition which took place in late September 1979 in Hong Kong. Around 10,000 medallions were minted, weighing 14 g each and containing 89 % Ag.

## 2.7. New influences on silver demand

Since 1974, speculative demand for silver is playing a major role on the market. Speculation in silver always existed, but it was usually a rather temporary phenomenon linked to the expectation of price changes arising from a market unbalance. However, since a few years several factors not specifically related to the silver market, are making of silver a monetary commodity beside an industrial commodity. Inflation and the confusion of the international monetary system are inducing investors to turn to commodities to protect themselves from the erosion of their currency and their wealth and, in this respect, silver is getting more important.

It is not possible to quantify the share of silver demand of speculative nature. It occurs primarily on futures market such as the COMEX and the LME and has a significant impact on prices as far as the bulk of such demand is conveyed by large commission houses. This does not necessarily imply that private physical stocks are being accumulated as these commission houses are most of the time dealing with paper transactions. A much smaller share of the speculative demand arise from the fact that small investors buy silver coins and commemoratives to protect themselves from inflation, although numismatic coins should not be considered as the ideal instrument for hedging on speculative operations since they are generally sold at a high premium over their silver content.

## 2.8. Silver demand outlook in the EEC

Table 2.8 a. summarizes the 1978 structure of silver consumption in the EEC countries. No data were available for the Netherlands or for Denmark and Ireland; silver demand in those countries is believed to be rather low and is

Table 2.8.a. 1978 SILVER CONSUMPTION IN EEC COUNTRIES

| End-uses | E E C | | Belgium | | France | | W.Germany | | Italy | | United Kingdom | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | mtAg | % | mtAg | % | mtAg | % | mtAg | % | mtAg | % | mtAg | % |
| Photo industry | 1588 | 41 | 558 | 90 | 248 | 36 | 213 | 26 | 162 | 20 | 407 | 45 |
| Elec-Electronic industry | 587 | 15 | 6 | 1 | 138 | 20 | 131 | 16 | 105 | 13 | 207 | 23 |
| .contacts and electronic components | n.a. | | n.a. | | 123 | | n.a. | | 105 | | 167 | |
| .batteries | n.a. | | n.a. | | 15 | | n.a. | | - | | 40 | |
| Brazing alloys & soldering | 496 | 13 | 25 | 4 | 117 | 17 | 90 | 11 | 129 | 16 | 135 | 15 |
| Jewelry and Silverware | 800 | 20 | - | - | 180 | 26 | 205 | 25 | 388 | 48 | 27 | 3 |
| Other industrial uses | 429 | 11 | 31 | 5 | 7 | 1 | 182 | 22 | 25 | 3 | 126 | 14 |
| Total industrial uses | 3900 | | 620 | 100 | 690 | 100 | 821 | 100 | 809 | 100 | 902 | 100 |
| Coinage | 457 | | - | | 345 | | 112 | | - | | - | |
| Total consumption | 4357 | | 620 | | 1035 | | 933 | | 809 | | 902 | |

estimated at 58 mt Ag included in the quantity representing the "other industrial uses" although it is assumed to be related essentially to electric-electronic uses.

Tentative forecasts of the 1985 demand situation are presented in table 2.8.b. They are based essentially on several considerations connected with each of the major end-use sectors taking into account the potential impacts of the technological changes presently occurring.

- <u>Photography industry</u>

  The industry is expected to grow at an average annual rate of 5 % which should, however, not induce a similar growth in new silver consumption because of

  - . the improved efficiency of the manufacture processes;
  - . the extension of used photographic products recycling;
  - . the substitution of silverless reprohraphy processes;
  - . the development of new technologies requiring less or no silver.

  The above factors should balance the increase in total silver needs linked to the growth of the sector and reduce silver consumption growth in the photography industry to 1 % per year up to 1985, and even 0 % thereafter.
  In addition, the re-organization of Kodak's production among France and the UK will result in a slight "above trand" increase of the French consumption and a corresponding decrease of the British consumption by 1982.

- <u>Electric-electronic industry</u>

  Two factors should affect the use of silver in <u>electrical contacts</u>:

  the replacement, in the telephony sector, of electro-mechanical contacts by electronic ones; this will reduce by a factor 3 the total amount of silver used in the sector, and by a factor 10 the total silver requirements for each new line installed;

for instance, in France, the telephone industry consumed 30 mt Ag in 1977 and its total Ag requirements are not expected to exceed 10 mt in 1985;

the generalized use of Ag-plated contacts instead of massive silver contacts; nonetheless, more and more applications will require control units and switchboard gears, thus increasing the total demand for contacts.

The demand for silver in electrical contacts is therefore expected to decrease up to 1985 and to increase slightly afterwards when telephony has completed the transfer to electronic contacts and when the volume growth in the sector will no longer be balanced by to-day's ongoing technological changes.

In the field of electronic components, a long-term growth rate of 10 % per year might be expected because of the increase of electronic applications and the replacement of electromechanical contactors by electronic contactors using Pt, Pd and Ag. This high growth rate will, however, not result in a significant increase of the silver demand since electronic components are currently consuming less than 1 % of the total silver demand.

As far as batteries are concerned, it should be distinguished between military use batteries and button cells.

Silver demand for military use batteries is linked essentially to military programmes and such currently ongoing programmes should induce a 4 % per year increase of Ag requirements up to 1985.

As to button cells, two factors have opposite effects :

- the unit consumption of silver could be reduced if current strength may be reduced, and lithium and zinc rival Ag in LCD and LED;
- more and more applications requiring button cells are developing (electronic watches, non-rechargeable extrathin calculators, microprocessors, microradios, cigar lighters...).

The net effect of both influences should allow an increase of Ag demand from the sector, so the more that button cell production should develop in the EEC, notably from Berec Micro Batteries in the United Kingdom where production started in 1978 and is expected to grow at a 20 %/year rate over the next 5 years.

- Brazing alloys

  The general trend in the brazing alloys sector points to a stabilization or even a decrease of silver use in the long run. There are many reasons to such an evolution :

  . use of preformed brazing alloys;
  . automation of brazing processes (5 % in the UK);
  . lower Ag content of common brazing alloys;
  . development of new technologies removing the need for brazing.

  Several of the above factors imply a higher efficiency of the brazing operation and thus a lower consumption of brazing alloys or a lesser requirement in terms of silver content.

  Antipollution and safety regulations requiring higher Ag content in some brazing alloys could restrain the decrease of specific consumption of silver by the sector

- Jewelry and silverware

  The future of silver consumption in jewelry and silverware depends on nothing else but tradition, standard of living and fashion. The most sensible forecast in this respect is a zero growth rate.

- Minor uses

  Strong growth of silver demand should be expected for mirrors if solar energy systems are being widely developed, not necessarily for domestic uses but for export.

  Silver use in catalysts will certainly keep on growing in the petrochemical and organic chemistry sectors which are estimated to progress at a 4 %/year rate.

- Coinage

  Since the rationale behind coinage programmes is quite independent of market considerations, it is very difficult to estimate what the EEC silver demand for coinage will be by 1985. However, assuming that Ag-coin minting programmes be maintained in France and Germany for commemoratives mainly intended for small investors, the total 1985 EEC silver demand for coinage is estimated at 350 mt.

Table 2.8.b. should be complemented by a few specific remarks :

(i) French silver consumption by the electric-electronic industry would break down as follows :

| | |
|---|---|
| 100 mt Ag | for contacts |
| 10 mt Ag | for electronic components |
| 5 mt Ag | for button cells |
| 20 mt Ag | for military use batteries. |

Similarly, the breakdown of British silver consumption by the same industry would be :

| | |
|---|---|
| 155 mt Ag | for contacts and electronic components |
| 40 mt Ag | for button cells |
| 35 mt Ag | for military use batteries. |

(ii) The use of silver in the UK in 1978 for jewelry and silverware was rather low (27 mt Ag) facing the expected 1979 consumption (66 mt Ag); therefore the UK forecast for 1985, which should be based on a zero growth rate as compared with the other EEC countries, is in fact estimated at an intermediate level of the 1978 and the 1979 consumptions, i.e. 50 mt Ag.

(iii) There ought to be a relatively sharp increase in the silver consumption for "other industrial uses"; such progress is linked to the assumption that the production of solar energy systems as well as of chemical and petrochemical applications would develop.

| Table 2.8.b. | THE 1985 OUTLOOK FOR SILVER CONSUMPTION IN THE EEC (mt Ag-yearly growth from 1978) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| End-uses | E E C | | Belgium | | France | | W.Germany | | Italy | | United Kingdom | |
| Photo-industry | 1690 | +0.9% | 590 | +0.8% | 300 | +2.8% | 230 | +1.1% | 170 | +0.7% | 400 | -0.2% |
| Elec-Electronic industry | 600 | +0.3% | 5 | -2.6% | 135 | -0.3% | 140 | +1.0% | 90 | -2.2% | 230 | +1.5% |
| Brazing alloys & soldering | 500 | +0.1% | 25 | 0% | 120 | +0.4% | 90 | 0% | 130 | +0.1% | 135 | 0% |
| Jewelry & Silverware | 825 | +0.4% | | | 180 | 0% | 205 | 0% | 390 | 0% | 50 | 0% |
| Other industrial uses | 565 | +4.0% | 35 | +1.7% | 30 | +23% | 235 | +3.7% | 35 | +2.6% | 160 | 3.5% |
| Total industrial uses | 4180 | +1.0% | 655 | +0.8% | 765 | +1.5% | 900 | +1.3% | 815 | +0.1% | 975 | +1.1% |
| Coinage | 350 | | | | | | | | | | | |
| Total consumption | 4530 | +0.6% | | | | | | | | | | |

(iv) The breakdown of the total EEC silver consumption by uses would not change drastically from 1978 to 1985; the share of "other industrial uses" would slightly increase in view of the progress of this item in France, West Germany and the United Kingdom.

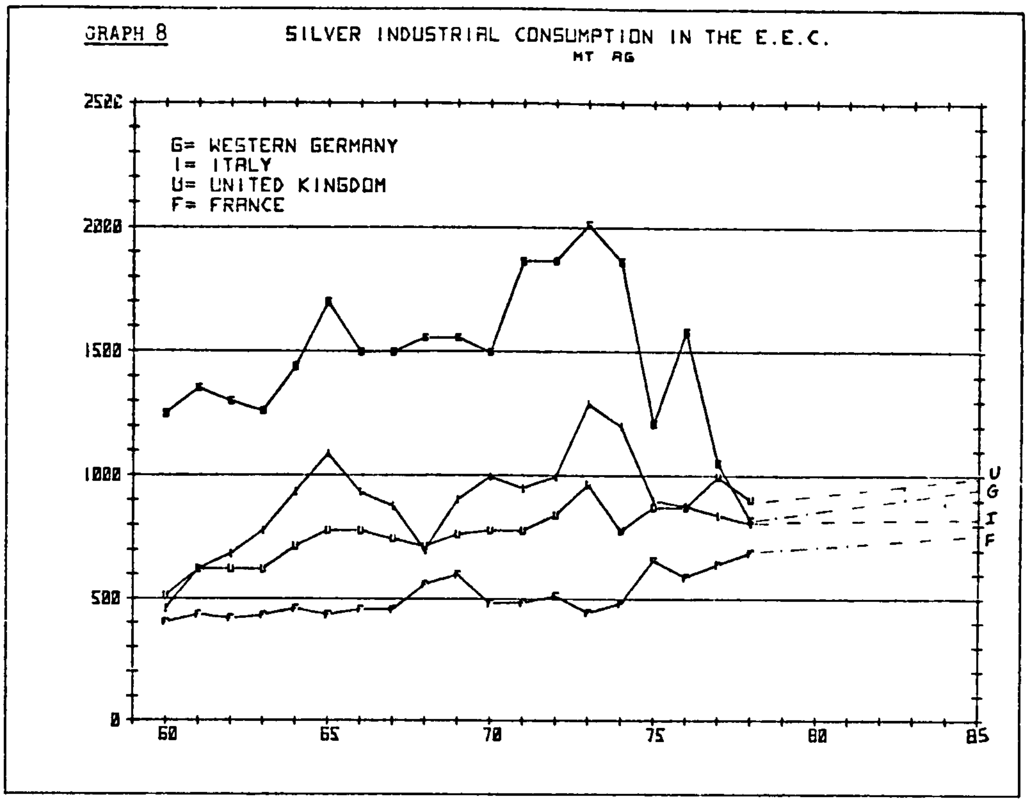
EEC silver consumption by uses
(% of total consumption)

| Consuming sectors | in 1978 | in 1985 |
|---|---|---|
| Photography industry | 41 | 40 |
| Electric-electronic ind. | 15 | 14 |
| Brazing alloys | 13 | 12 |
| Jewelry and silverware | 20 | 20 |
| Other industrial uses | 11 | 14 |
| | 100 % | 100 % |

(v) The silver consumption in Denmark, Ireland and the Netherlands is estimated to grow at an average annual rate of 2.7 % and could reach 70 mt Ag in 1985; this tonnage is included in the EEC consumption figures for "other industrial uses".

Graph 8 places the above forecasts in connection with the past history of the industrial consumption in France, Italy, West Germany and the United Kingdom.

It must be reminded that the silver consumption time series for West Germany is distorted by statistical errors consisting mainly in overestimation in 1973-1976 and underestimation in 1977-1978.


GRAPH 8 SILVER INDUSTRIAL CONSUMPTION IN THE E.E.C.
MT AG

It is interesting to compare the contingent forecasts presented above and those resulting from the extrapolation of the 1960-1978 trends, starting from the 1978 consumption figures. This exercise is relevant only for France, Italy and the United Kingdom since the trend estimate for West Germany seemed to be altered by statistical errors in the consumption time series.

Table 2.8.c. - 1985 expected Ag consumption by the EEC industry

| | Contingent estimates | | Extrapolated trend values | |
|---|---|---|---|---|
| | mt Ag | implied yearly growth rate (%) | mt Ag | 1960-78 yearly growth rate (%) |
| Belgium | 655 | 0.8 | - | n.a. |
| France | 765 | 1.5 | 815 | 2.4 |
| West Germany | 900 | 1.3 | - | not relevant |
| Italy | 815 | 0.1 | 949 | 2.3 |
| United Kingdom | 975 | 1.1 | 1,080 | 2.6 |
| Total EEC | 4,180 | 1.0 | - | n.a. |

Table 2.8.c. clearly evidences that the contingent forecasts imply a slowdown of the consumption growth rate which is consistent with the slowdown observed on a world level since the early 70's.

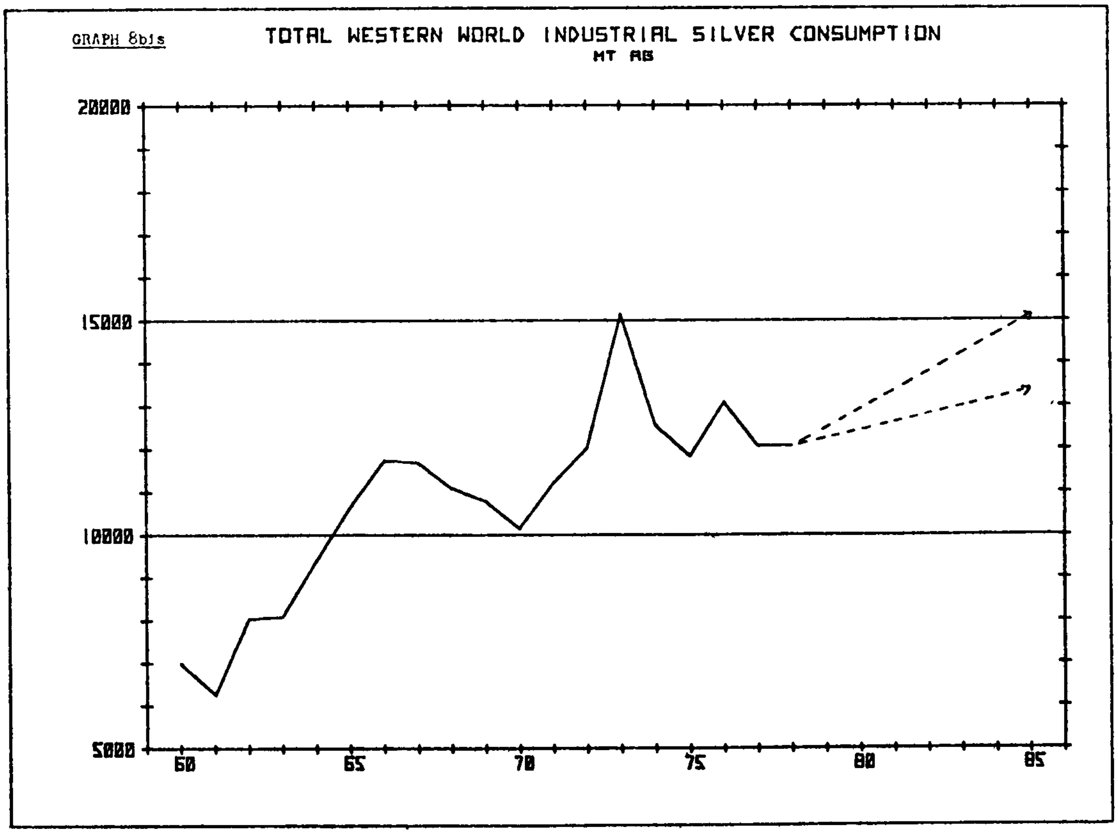
## 2.9. 1985 World silver consumption

1985 Silver consumption forecasts at the world level should be based on a detailed analysis of the major consuming sectors in the USA and in Japan, as well as in the EEC.. This being outside the scope of the present study, trend extrapolations of the non-communist silver demand have been calculated so as to propose a forecast range for 1985 silver consumption which, at least, ought to be consistent with the recent past.

At the beginning of chapter 2 it is shown that the world industrial silver demand growth slowed down over the 70's, decreasing from 6.4 % per year over the period 1960-69, to 1.4 % per year during the 70's. The overall annual growth rate over 1960-78 is 3.3 %.

Considering the the slowdown of the industrial silver consumption growth over the period 1970-78 partly reflects the exceptional downturn linked to the 1975-76 recession, the extrapolation of the 1.4 % growth rate up to 1985 should be viewed as a lower limit forecast, while the upper limit should be determined by the extrapolation of the long-term trend of 3.3 %.

Graph 8bis positions both 1985 extrapolations with reference to past history; trend extrapolations have been calculated based on the 1978 actual silver consumption in the industry and result in a 13,300-15,150 mt Ag range in 1985.



Silver consumption for coinage is assumed to keep an approximate share of 5 % in the total consumption, this is in line with the decreasing trend shown by coinage use since the mid-60's, and would position silver demand for coinage at around 800 mt Ag by 1985.

# Chapter 3 - PRICES and MARKET EQUILIBRIUM

# 3. PRICES and MARKET EQUILIBRIUM

## 3.1. Price definition and Metal Exchanges

Silver is traded on commodity markets in many places all over the world, the most important ones being the London Silver Market and the London Metal Exchange in the United Kingdom, the New York Commodity Exchange and the Chicago Board of Trade in the USA.

The prime function of a commodity market, in terms of its value to international economics, is to provide traders with a means of protecting themselves against adverse price fluctuations for the duration of any physical contract in which they are involved. The so-called "hedging" operations are realized through the purchase or sale of futures contracts; futures transactions are paper transactions which do not involve change of ownership or physical handling of the commodity. The futures transactions as well as the physical operations taking place on the Exchanges are the immediate determinant factors of the day-to-day price quotations.

The London Exchanges play a leading part in price fixation for European transactions, although the London and the US Exchanges mutually interact and thus follow a similar evolution pattern.

### 3.1.1. The London Exchanges

The London Metal Exchange is dealing in a limited number of commodities : copper, zinc, lead, tin, silver and, more recently, aluminium and nickel.

As is the case for most of the Exchanges, the advantages of the LME are threefold.

- Firstly, it enables producers to sell their products at any time and in any quantity, at a fair market price.
- Secondly, it provides fabricators and manufacturers with the facility in purchasing supplies of raw materials at all times.

Thirdly, it provides official daily quotations, recognized throughout the world as representative of the free interaction of market forces.

Dealings on the LME are done orally by "Ring dealers" firms (Cfr. appendix 5) who are seated in a circle and make bids and offers to each other across the Ring. Prices fluctuate up and down, according to whether buyers or sellers predominate. A deal is immediately concluded when a bid or an offer is accepted. This is checked at the end of the session by the clerks of the firms concerned and contracts are exchanged before noon on the following day. The client's contract is normally sent the same day.

Silver is traded separately from the other metals during two 5-minute sessions per Ring sitting; there are two Ring sittings each day : one at noon and one in the afternoon.

The closing prices of the second session in the morning are known as the official prices which are agreed by the "Fixing Committee" and publicly announced. Although dealings in the afternoon are transacted in the same manner as in the morning, no prices are announced and no "official prices" are given.

Silver positions may be held up to seven months forward and prices are officially quoted for cash and for 3 months. The final day for liquidation of a position is the last market day before the date of maturity.

The _London Silver Market_ consists of three long-established bullion brokers : Mocatta & Goldsmid Ltd., Samuel Montagu & Co. Ltd. and Sharp & Pixley & Co. Ltd.

They get together every day at noon to fix a price for transactions; there is no time limit to their meeting. The price they fix must be such that all effective offerings for sale can be absorbed, and selling orders received in time are then executed at the fixed prices. It may happen that offerings at the fixed prices be insufficient to satisfy the buyers, whereas higher prices would have produced more selling orders which, in turn, would have made it impracticable to fix at the higher level; on the contrary, there may be an excess of buying over selling orders at the fixed prices: in such circumstances, the broker may not always be able to execute buying orders fully at the fixed prices.

The London Silver Market is more important than the LME because most of the physical transactions are taking place on the LSM and thus the prices fixed at the LSM are accepted all over the world.

### 3.1.2. The US Exchanges

Trading in silver futures in the USA is conducted on the New York Commodity Exchange and the Chicago Board of Trade. The Comex is the most important of the two.

Silver brands designated by the Comex for delivery against contracts on the Exchange are not necessarily high quality silver since the Comex' requirements are limited to a minimum silver content of 99.9 %, without any reference to impurities. (The ASTM specifications set maximum limits on impurities.)

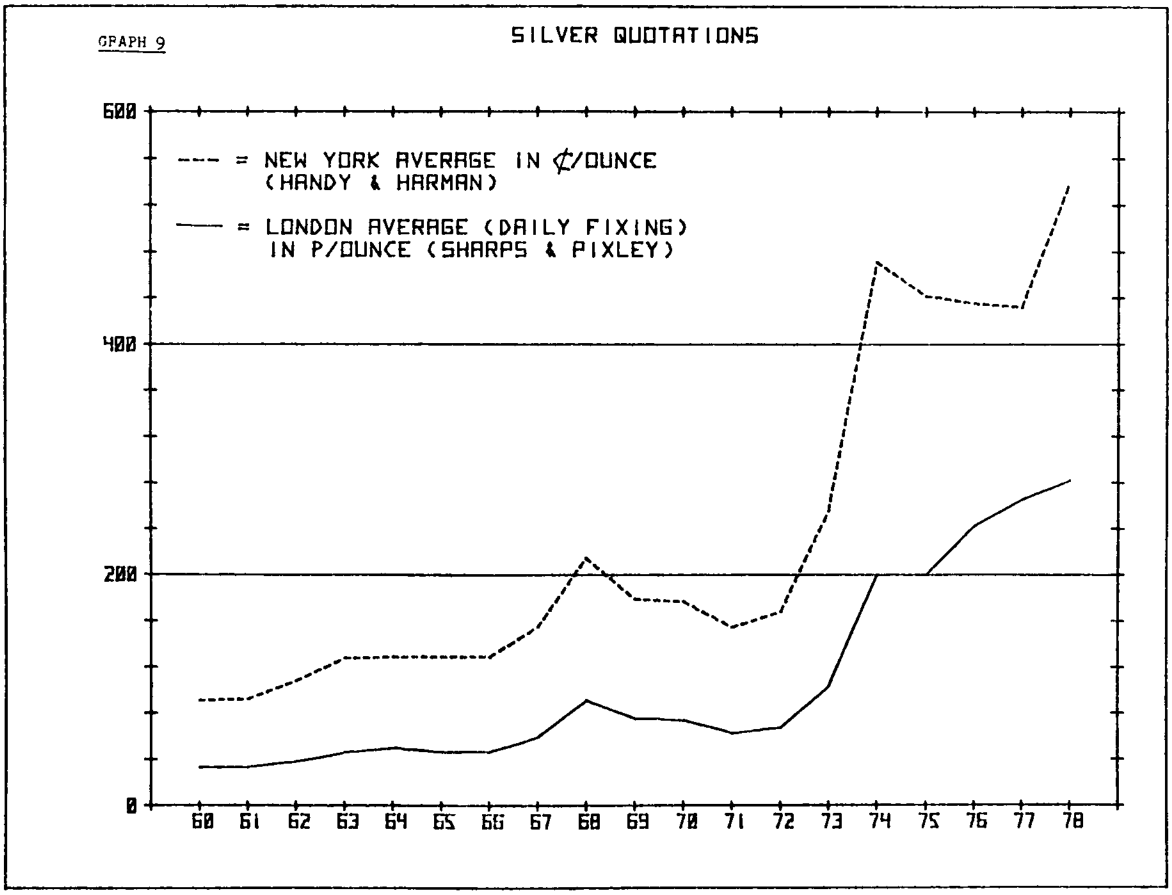
Therefore, when Comex inventories come down to low levels, it becomes more and more difficult to select acceptable ingots for delivery to industrial buyers; the low quality ingots have to be upgraded and the net price paid by the industrial user is in fact the Comex' price plus some refining charges. This accounts for the difference between the Comex' price and the price published by Handy & Harman, one of the largest merchants and silver refiners in New York. The H & H's price reflects the lowest price at which Handy & Harman can obtain offers for silver in commercial shape of acceptable quality, for delivery in New York, in quantities sufficient to meet its requirements. Thus the Handy & Harman's price is closely related to the Comex' price, but it also reflects the quality of silver availabilities and is generally higher than the Comex price. It is published at noon, on each working day.

## 3.2. Silver price fluctuations over the last twenty years

Although largely used for coinage up to the mid 60's, silver was considered primarily as an industrial commodity up to the early 70's; hence, the long-term Ag price evolution basically reflected the supply/demand balance of the market. However, several economic factors developed since the end of the 60's that gave silver the status of investment commodity and thus induced a growing and continuous speculative activity on the silver markets, such activity having usually a disturbing impact on the commodity price.

Graph 9 shows the silver price fluctuations over the period 1960-1978, both on the New York market and on the London market.

The bullion brokers' price of London (LSM) is indeed the most relevant price for the European market although silver prices follow a similar evolution pattern on all the Exchanges since silver is openly and internationally traded.



During the early 60's, the silver price fluctuations induced by the supply/demand situation of the market were smoothed through governmental action initiated essentially in the USA.

The US Government's policy was aiming at a price stabilization which it successfully achieved up to 1967. The US Treasury mastered the governmental actions on the US market and its activity contributed to isolate, to some extent, the New York market from the other world markets; nonetheless, the importance of the US silver consumption at a world level allowed the US Government's action to have, indirectly, a moderating influence on price fluctuations on the other markets. From 1963 until May 1967, the US Treasury maintained the silver price at $ 1.29 per oz, purchasing silver surplus or selling "free silver" to home users when needed. This was possible in view of the availability of important silver inventories which were built largely through the redemption of silver certificates. An example of a more specific action conducted by the Treasury is the Coinage Act of 1965 which cancelled the use of silver in the minting of the 90 % and the 40 % Ag half-dollar coins. This induced a sharp drop in the quantity of silver used for coinage in the USA during the following years and helped maintain the availability of metal for industrial purposes. In 1967, the Treasury "free stocks" were no longer large enough to satisfy its actions; more stringent purchase terms were imposed and the quality of the silver offered for sale rapidly deteriorated. Industrial users thus turned to the market Exchanges, inducing an upsurge of non-Treasury silver prices and active speculation. The Treasury discontinued to sell at the $ 1.29 price. Silver sales by the US Government completely stopped in 1970.

Much less decisive actions were and are still conducted by governments through the national banks. They consist in minting or demonetization programmes , the immediate effect of which is to reduce or increase the silver availability to industrial users. The actual impact of these actions on prices depends largely on the total amount of silver involved and on the current supply/demand situation. For instance, Peru and Mexico have presently started minting programmes which partly aim at maintaining the world silver price at high levels by reducing the supply to industrial users.

When the US Treasury abandoned its long-standing market stabilization policies in 1967, speculators' and investors' influences started to weigh on the market. With the generalizing loss of confidence in world currencies, silver became a common devaluation hedge and its status of investment commodity started to develop. Hence, in 1968, speculation linked to gold and to the major currencies (£ and $) pushed the silver price to all-time high in constant monetary units, and divestment by speculators and investors maintained thereafter a downward pressure on the price, up to the early 70's.

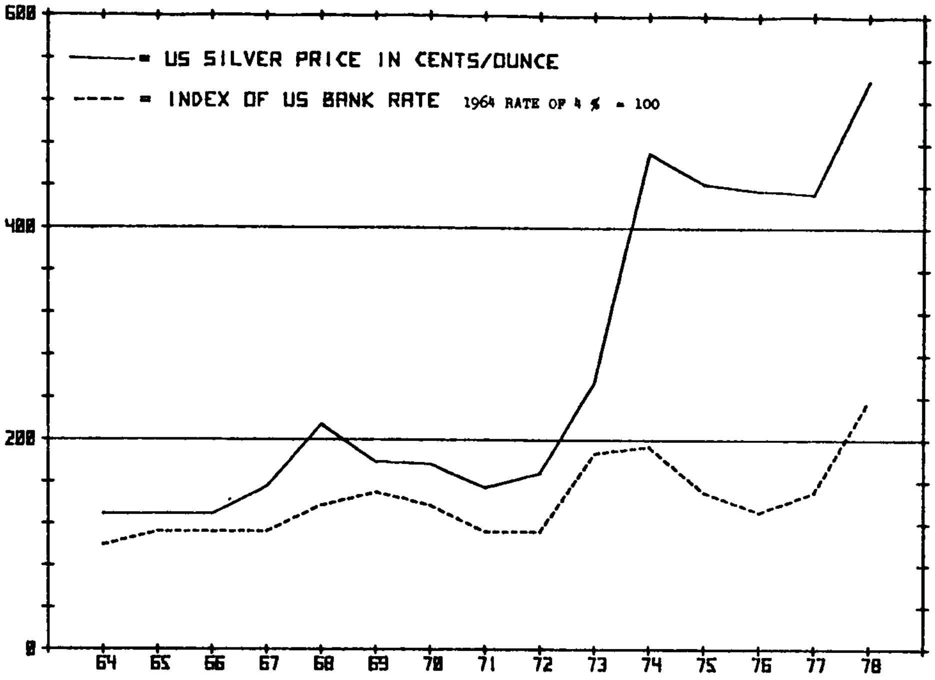
During the 70's, widespread and uninterrupted inflation intensified the role of silver as second hedge commodity after gold, so that the persistent decline in purchase power of paper currencies became one of the major driving forces behind the upward movement of silver prices over the last years.

Two graphs may emphasize the growing role of silver as investment commodity (as gold) and bring out the causal relationship between silver price fluctuations and speculative activity linked to currencies instability and inflation.

- Graph 10 compares the price evolution of silver in the USA with an index value of the US bank rate, the correlation between both series is fairly high (0.76 over the period 1964-78), a similar correlation was detected between the London silver price and the UK bank rate (0.64 over the same period).

GRAPH 10

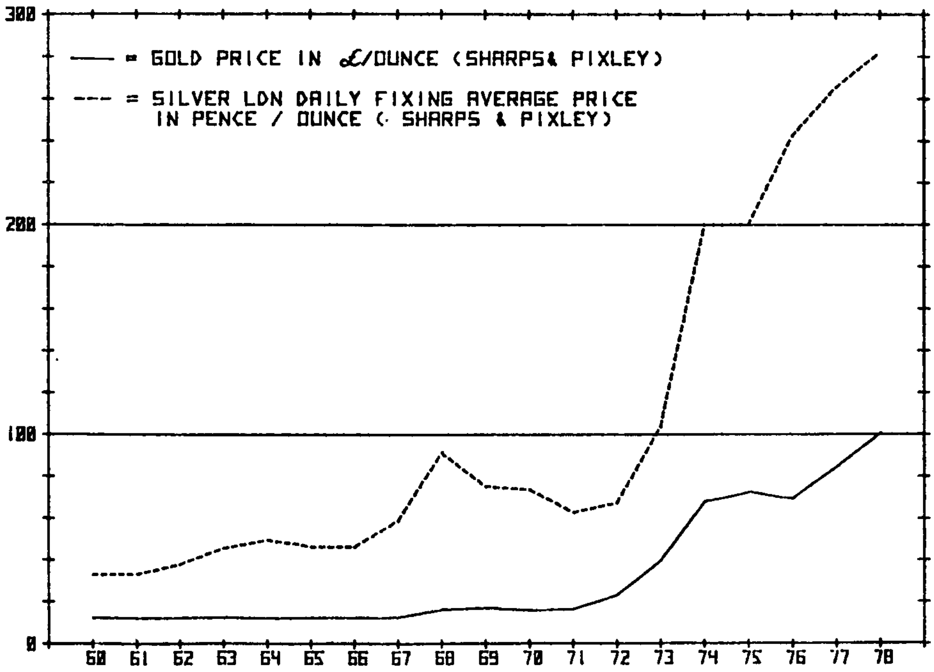
US SILVER PRICE & INDEX OF US BANK RATE



- Graph 11 parallels the evolution of the price of gold and the price of silver, the correlation between both series is again quite high (0.98 over the period 1960-78).

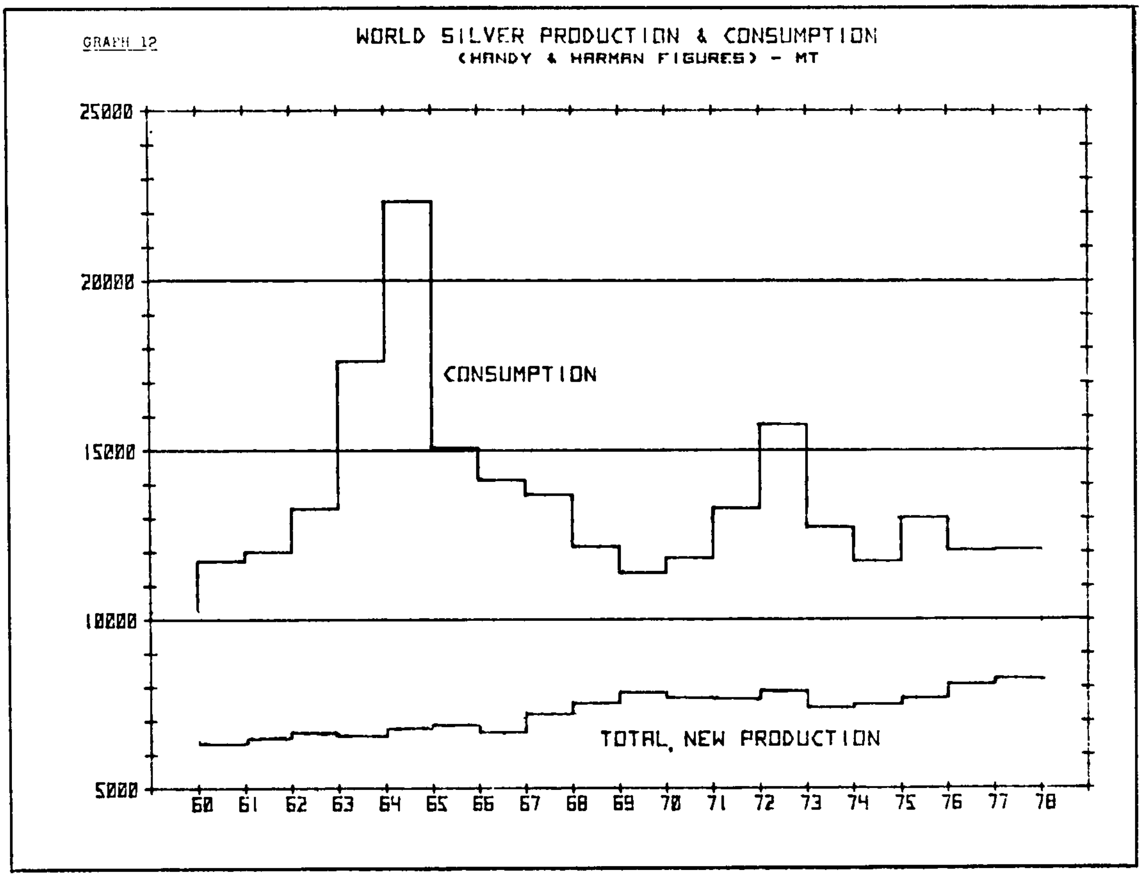
GRAPH 11

GOLD & SILVER PRICES

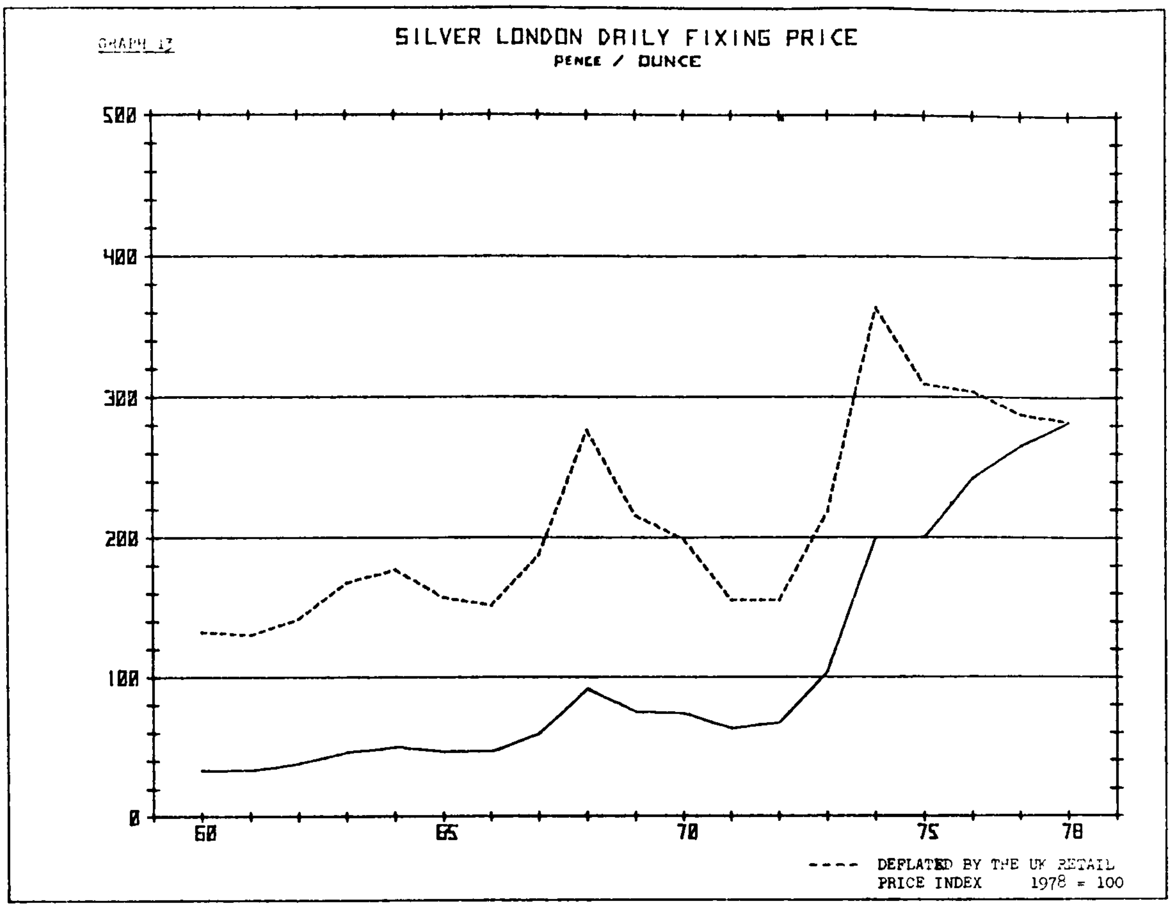


## 3.3. The supply/demand balance and the long-term trend in prices

Over the years, there has always been a deficit between silver consumption needs and primary silver production, this deficit being made good by secondary silver sources (Cfr. graph 12).



The basic scarcity of new silver supply is the determinant factor that brought about the rising trend observed in the long-term evolution of the silver price. Over the period 1960-78, the London silver price has been growing at an average annual rate of 12.8 %, which, however, drops to 4.7 % if prices are expressed in constant £ as shown in graph 13.



GRAPH 17

SILVER LONDON DAILY FIXING PRICE
PENCE / OUNCE

## 3.4. Silver price outlook

Two basic influences should play a role in the future price evolution :

- the adequacy of silver supply to industry needs
  and
- the speculative activity on silver regarded as an investment commodity and a hedge against inflation and monetary depreciation

The 1985 outlook of the supply/demand balance on the silver market is rather difficult to specify, since primary silver supply will continue to show a deficit with respect to silver demand, and the availability of secondary silver will still largely depend on price considerations.

Table 3.4.a. gathers the forecast range proposed for primary silver production and for silver consumption at the world level.

Table 3.4.a. - (mt Ag)

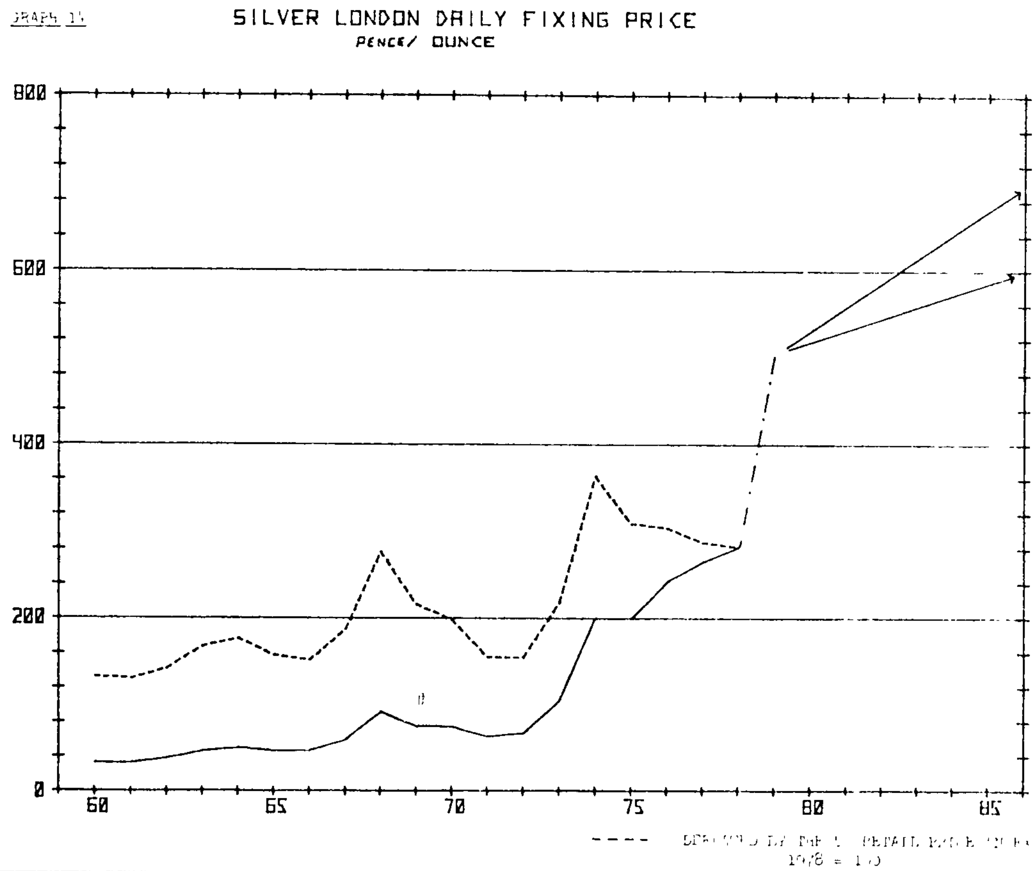
| | World supply of primary silver | World silver consumption | | |
|---|---|---|---|---|
| | | industrial | coinage | total |
| 1978 reference | 8,242 | 12,068 | 1,089 | 13,157 |
| 1985 estimates | 9,370 | 13,300 | 800 | 14,100 |
| | 9,550 | 15,150 | 800 | 15,950 |

Primary silver production could satisfy as much as 60 to 65 % of the world total silver needs by 1985; the present share of primary silver in the total supply is 62 %, therefore, no significant worsening of the fundamental supply/demand deficit is to be feared up to 1985. Secondary silver sources should make good the deficit which could range between 4,730 and 6,400 mt Ag in 1985. The structure of the secondary supply would widely vary according to the assumptions made on the availability of Indian silver and of the GSA's silver stockpile. The higher the quantities made available by these sources, the lower the pressure on the industrial scrap supply; in this respect, moderately optimistic assumptions on the Indian and the GSA's availabilities would imply that 20 to 25 % of the total silver needs should be satisfied by industrial scrap; obviously, this proportion would increase, should the ban on Indian silver exports be maintained and should the GSA not release its huge stockpile. Presently, industrial scrap accounts for 20 % of the total silver supply.

Considering the above, the silver price is bound to keep growing over the foreseeable future, since only a price increase may lead to the release and the reclaiming of the required above-ground silver resources.

However, the level the silver price would reach in 1985 would not only reflect the rising trend linked to the long-lasting market imbalance, but would also be positioned with respect to a new "plateau" determined by the recent surge on silver as an investment and speculation commodity. Speculation is raising the silver price to an estimated average of 500 pence per ounce in 1979; present highs of 800 pence/ounce seem unbearable to the industry, if maintained over a long period, and it would be sensible to disregard those exceptional levels when estimating the 1985 prices.

In view of the speculative activity now developing considerably on the silver market, tentative forecasts for the mid 80's should be regarded merely as price indications consistent with the fundamental price trend (+ 4.7 % per year in constant £) and with the new price "plateau" brought on by active speculation. It is thus suggested that the silver price should fluctuate around 700 pence/ounce as shown in graph 14, 600 pence/ounce being a lower limit.



# Chapter 4 - THE SUBSTITUTION POSSIBILITIES - - INVESTIGATIONS TO BE MADE - TECHNICAL AND ECONOMIC ASPECTS

The future of silver demand will depend on technical, technological as well as economical evolutions; some of these will develop on their own and will lead to an increase or a decrease of the silver demand, others will have to be helped to lead to a reduction of the silver demand through substitution.

These substitution actions may be classified in 4 types, according to whether it is a question of substituting the application techniques, substituting another material for all or part of silver, substitution of technology and lastly substitution of the recovery process.

## 4.1. SUBSTITUTION OF APPLICATION TECHNIQUES

The fundamental technologies used are not called into question again (as in par. 4.1.3.), but a better use of silver is sought for.

### 4.1.1. In the photography field

Research and development works continue with the various international groups producing sensitive surfaces, with a general view to reducing the specific consumption of silver; this can be obtained in several ways :

- improvement of the quantum efficiency of emulsions by introducing more effective sensitizers; thus, in the past, sulphur was replaced by gold, involving considerable gains in sensitivity; one may imagine that improvements are still possible and research is still in progress in this field;
- reduction in the thickness of emulsions through an improvement of the coating method which comes under the fluids technique; this thickness has already been reduced, but works aim at lowering it still further;

- reduction in scrap and flaws arising during the manufacturing process; it was noted that the quantities of new scrap processed per year are quite considerable and contain hundreds of tons of silver; the photography industry is constantly seeking to reduce these scrap and flaws and, although improvements were already reached, progress can still be made by substitution of the manufacturing process.

To conclude, a reduction in the specific consumption of silver of around 2 to 3 % per year was already reached by the photography industry and this should continue further at a similar rate between now and 1985 at least; this reduction stabilized the demand for silver whilst it increased the production (in surface) of sensitive surfaces, and should allow this stabilization to continue. After this date, it is possible that a minimum technical threshold of specific silver consumption will have been reached.

The photography industry itself (or universities in the case of research for more effective sensitizers) undertake research and development work in this field. In view of the competition existing in this industry and the concentration of the companies, the research and development works are kept jealously secret by the photography industry which does not want to indicate the state and content of its research.

### 4.1.2. In the electrical and electronic contacts field

The history of the different contact technologies (in chronological order of development) developed as follows :

- solid silver rivets;
- silver plated on a support in the form of a cuprous rivet to obtain bimetal or trimetal composites;
- solid silver buttons soldered to the contact blade and no longer riveted;
- bimetal buttons obtained by powder technology.

This evolution provided a substantial silver economy (around 70 %).

The three first technologies exist and are more or less currently used; the fourth technology was developed by some contact producers (and refiners) but does not seem to be much widespread.

A first research theme would be to develop the knowledge and the application of sintered powder metallurgy in the electrical contact field.

A second research theme of more general interest would be the study of silver deposition processes on a substratum of common metal (in this respect, processes using other techniques than galvanoplasty could be investigated).

A third research theme would aim at improving the physical characteristics of existing contacts by application of a hardening process of the contact materials.

These two last themes, which form a part of a vast research programme (other elements of which are to be found in par. 4.2.2.), could be undertaken with the help of the EEC by centralized laboratories of the electrical industry, such as the Electrical Research Association (ERA), Great Britain, the Laboratoire Central des Industries Electriques (LCIE), France, or other research centres in the EEC.

Application of these new technologies will certainly bring forth financial problems of investment to contact producing companies.

It would appear that the contacts (generally speaking) are not adapted to each use for economic and technical reasons, and that the parts are frequently overdimensioned : for example, a contact was designed and dimensioned to work 10,000 times where it is used 1,000 times only. Therefore, the demand for silver could be reduced by reducing the overdimensioning of the parts, but the manufacturing and the distribution costs would be considerably higher; thus it does not seem interesting to study this aspect in the research programme.

In the case of electronic components, new techniques in connection with the use of silver are also investigated (non-priority study in view of the small percentage of silver demand concerned).

### 4.1.3. Brazing field

Three substitutions of application techniques have started and could lead to silver savings in the short term if encouraged. They are :

- Development of pre-forms fitted to the form of each part to be brazed; this development could be widened thanks to publicity on the one hand, and to conception and development of new shapes in cooperation with clients, on the other hand.
- Development of the use of furnaces instead of a flame in order to use the exact quantities of brazing required, to set the temperatures better and, if required, to increase it so as to reduce the silver content of the alloys.
- Development of the automation of the process of brazing parts using a precision machine-tool and a brazing paste. The precision machine-tool used enables silver savings at various levels :
  - economy of raw materials : on the one hand, reduction in the specific brazing consumption, and hence of silver, of around 20 % or more, through depositing the brazing at the required points only (automatic feeding of the part); on the other hand, the more precise setting of the temperature and its possible raising as compared with manual brazing, may reduce the silver content of the alloy used;
  - economy of energy : the reduction in the surface coated together with the replacement of propane by acetylene on certain machines would enable the energy costs of the operation to be halved;
  - gains in productivity : in the case of certain parts, the production rates can be doubled.

These automatic machines are being developed by several firms, some of them producing brazing, the others producing machine tools with the help of users. Their use is recent, still very little widespread and it still involves numerous technical problems which deserve to be solved; moreover, the development of a machine adapted to each case appears to be necessary.

These processes require the development of a range of paste and "fluxes" with different characteristics and different silver contents, parallel to those of the alloys presently available in the form of wires and beads.

## 4.2. SUBSTITUTION OF ANOTHER MATERIAL FOR ALL OR PART OF OF THE SILVER

### 4.2.1. Case of photography

Being exceptionally sensitive to light, the silver halides seem irreplaceable in instantaneous photography; in return, when the exposure time can be increased (copies, graphic arts, microfilms), other photosensitive materials can be used, but their use remains limited in view of their limited quality :

- diazos or vesicular recording processes, for example, are used in copies of drawings and certain licrofilms, with a limited resolution capacity;
- photopolymers and bichromate gelatines are used notably in the graphic arts where the quality of the films and of the printing paper seems to be improved so as to be more widely used.

In the field of the colour photography, research and development do not seem to be really opportune : silver is used very differently and is fully recoverable in the treatment baths. In the medical radiography field, it will be emphasized that the trend to miniaturize the radiographies is in progress, either they have a smaller surface, or they are recorded on microfilms, this trend should possibly be encouraged but will not always result in a drop of the silver demand, but in an increase of silver rotation. Therefore, the research and development studies to be undertaken may be summarized as follows :

- generally speaking, improvement of the sensitivity of known non-silver photosensitive materials, definition and resolution capacity;
- improvement of films and photopolymer base printing paper along several lines :
  - . increase of the mechanical strength allowing a larger number of prints at higher speed;
  - . reduction of the wear of the photopolymer or of the subjacent layer, so as to avoid impairment of the picture;
  - . improvement of the adherence of the photopolymer to the undercoat;
- research in connection with other photosensitive materials; fundamental study undertaken both by the multinational groups (in this case, neither the state nor the content of the research and development in progress is known) and the universities and, in this latter case, it has to be aided.

### 4.2.2. Case of contacts

Here again, it is difficult to replace silver owing to its excellent electrical and thermal conductability.

The main directions of a research and development policy appear to be as follows :

- Fundamental study of the role of the filler elements such as CdO on the contact properties (in fact, the use of materials other than silver depends on experience). It would also be possible to turn to tungsten or tungsten carbide (the economy of which is also required). The aim of such a study is to increase the content of additive elements to reduce the silver consumption; it is also possibly a question of replacing the silver-cadmium oxide alloy used for strong current contacts, but polluting.

- Study of the impairment mode of contact materials with a silver base (under the arc effect).
- Study of the substitution of more usual materials for silver. This is a very important line of research that can lead to industrial results in the long-range.

It is essential that all this research work be carried out in a coordinate way and as a priority.

### 4.2.3. Case of batteries

In the army field, where optimum performances are required, a substitution would not appear desirable.

In the field of button cells, it is already known that it is possible to reduce the silver content and to increase that of manganese oxide to the prejudice of the intensity of the current obtained, while obtaining sufficient performances for certain new gadgets containing new displays which do not consume much current.

Therefore, it does not seem necessary to undertake studies in these fields.

### 4.2.4. Case of brazing

A more fundamental study would be the research about any substitute (metal or not) for silver in brazing; in some cases, results were achieved with phosphorus.

### 4.2.5. Other applications

#### Catalysts

One direction of a research and development policy could concern research about an economic substitute for silver but, as silver is not consumed, this study does not seem as interesting as others, knowing that its results are not bound to be successful.

### Mirrors

In the case of solar mirrors, research is in the hands of organizations and firms devoted to developing systems of capting solar energy.

### Silverware

In most uses (household silverware), silver is not technically indispensable, stainless steel can substitute for it; nevertheless, for essentially sociological reasons, it is difficult to contemplate to stop using it; anyhow, the relative share relating to this use will decrease.

## 4.3. SUBSTITUTION OF FUNDAMENTAL TECHNOLOGIES

### 4.3.1. In the field of photography

New technologies are developing in the different applications of silver sensitive surfaces and compete with them. Among others, should be mentioned :

- in the photocopy field, diazo and xerography processes have already replaced totally the silver process, with the exception of a few applications where a certain quality of definition is necessary;
- in the radiography field, the processes using electronics (scanners, thermography) and acoustics (echography) are complementary to X-rays; nevertheless, at a remoter date, a system using a magnetic tape will no doubt replace radiographies; its development is not yet complete and its cost still very high, but the miniaturization of electronics, the lowering of the foreseeable cost and the storage facility of informations portend a good future for this technology;
- in the non-professional motion picture field, video is starting to attack this market which should soon give way, with here again miniaturization, reduction in the foreseeable

cost together with obtaining instant pictures, and facility of use. The appearance on the scene of instantaneous development films where silver cannot be recovered in the bathis in the direction opposite to the improvement of silver supply;

- in the field of non-professional colour photographs, the extension of the use of Polaroïd-type instant photographs is also in the direction opposite to an economy in raw materials (especially silver).

It seems that Europe cannot do very much in connection with these technological evolutions which are ordered in the United States and Japan.

### 4.3.2. In the electrical-electronic field

The main substitution of technology concerns telecommunication where electronical switching replacing electromechanical switching reduces the global consumption of raw materials by a factor of about 10, and notably that of the silver used at contact level. This precious metal is to be found in infinitely lower quantities in the electronic components used (in increased quantity) in the new switching centres. Nevertheless, owing to the maintenance of the former system, the global demand for silver for this application will be divided by 3 only until about 1985.

In the electronics field, the miniaturization and the solid-state switching devices using platinum or palladium should in theory, and gradually, replace the mechanical silver contacts.

Here again, these technological evolutions are in progress and are self-producing; no action appears to be necessary at the EEC level.

### 4.3.3. In the brazing field

Other technologies to manufacture assemblies are already used by some constructors; for instance, in the automobile field, only Renault and Chrysler in France, for instance use silver brazing. In fact, one may conceive

- promoting new modes of assembly by using new technologies without brazing (bonding, friction assembly, etc .);
- promoting new materials (notably polymers as substitution for metal) in the traditional fields of application (automobile or building). These new non-metal materials can then be assembled in a quite different way.

## 4.4. MAINTENANCE POSSIBILITIES

### 4.4.1. In the field of photography

It is in this field that silver consumption is quite considerable and where recovery action is the most paying and most quickly accessible. Among these may be mentioned :

- substitution of an electrolytic process with re-circulation of the baths for the conventional electrolytic process, at least in the large laboratories; this new process has a recovery rate of around 95 % and the silver obtained contains more than 90 %; nevertheless, the limit to the profitability of these installations is high (in 1978 : 2.2 kg/month of silver as against 1.4 kg for conventional machines); the increase in the price of silver should favour the use of such machines, without any action other than advertising being necessary;
- development of the use of electrolytic machines to recover silver from the treatment baths, which the present price of silver would often pay; an incitement would be the application of antipollution regulation; a publicity action could be promoted;

- reduction in silver losses when treating wastes (incineration and smelting). It has been seen that the installation of filters and smoke washers can recover almost all the silver contained in the smokes from smelting furnaces and incinerators; this installation should therefore be made compulsory;
- reduction in losses in the waters rejected by the photography industry by introducing a process to recover the silver contained.

### 4.4.2. In the electric-electronic field

Certain products in this industry are recovered at the end of their service life, like the silver contained (case of batteries, certain electronic wastes containing also other precious metals, old computers, switching boards, above all); nevertheless, most of the silver used in this industry is lost. Adequate systems of recovery would therefore be most useful to develop, notably mechanical or electrochemical processes; there exists an important handicap due to the dispersion of contacts and electronic components in the finished products and the manual disassembly necessary (frequently at a prohibitive cost), before contemplating any recovery of the metals contained.

It should be noted that the use of plating or other technologies consuming less silver (instead of solid silver) in contacts, goes in the direction opposite to possibly increased recovery.

### 4.4.3. In the brazing field

Used in highly dispersed form, it would not appear to be possible to recover the silver at the end of the working life of the products (situation comparable to that of par. 4.4.2.).

# Chapter 5 - CONCLUSIONS and RECOMMENDATIONS

# 5. CONCLUSIONS and RECOMMENDATIONS

## 5.1. The 1985 outlook of the silver market

The breakdown of the supply on the silver market is presently as follows :

| 1978 | mt Ag | % of total supply |
|---|---|---|
| Primary silver production | 8,242 | 62 |
| Secondary silver production | 5,074 | 38 |
| of which : | | |
| Indian silver | 1,477 | 11 |
| coin melt | 435 | 3 |
| industrial scrap | 2,613 | 20 |
| stock changes | 549 | 4 |
| Total : | 13,316 | |

Primary silver production is largely linked to base metals production (Cu - Zn - Pb) in which Ag arises as a by-product. Mining projects relating to Ag ore deposits and base metals deposits together with the expansion plans at existing facilities, allow to estimate the 1985 primary silver production to be in the range of 9,370 - 9,550 mt Ag. The share of the EEC in this total would be insignificant and even lower than the present 2 % since no major silver-containing ore reserves are planned to be developed within the EEC countries by the mid 80's.

Secondary silver supply consists mainly of recycled industrial scrap and Indian silver. The so-called "above-ground resources" of silver always were an essential part of the total silver supply since primary production is basically insufficient to satisfy the total needs. The future availability of Indian silver is quite uncertain, as well as of US GSA silver stockpile, since both supply sources are ultimately managed by political authorities.

It is assumed that, in the future, the deficit of primary silver will continue to be balanced by secondary silver supply; depending on the total availability from India, inventories and coin melt as well as on the total silver requirements to be met by above-ground resources, industrial scrap is expected to gain a still larger share of the total silver supply (up to 25 % as a medium forecast).

Western world silver consumption reached 13,160 mt Ag in 1978; the industry currently generates more than 90 % of the total needs and coinage absorbs some 5 to 8 % of the silver consumed. As is the case for most of the base metals industry, the growth of silver demand from the industry slowed down since the early 70's, dropping from 6.4 % per year over the period 1960-1969 to 1.4 % per year during the 70's. Silver consumption forecasts for 1985 are based on the latter trend as a lower limit, and on the 1960-1978 overall growth rate of 3.3 % per year as an upper limit, as it may be assumed that the 1975-76 recession years had a major influence in pushing downward the growth rate of silver consumption of the 70's. Demand for coinage is assumed to keep an approximate share of 5 % of the total consumption so that the 1985 world silver consumption would be in the range of 14,100 and 15,950 mt Ag, the breakdown being as follows :

industrial uses - 13,300 to 15,150 mt Ag
coinage - 800 mt Ag.

In 1978, the EEC countries consumed an estimated 4,360 mt Ag, i.e. 33 % of the world total. The EEC as a whole is the second largest silver user after the USA (4,964 mt Ag in 1978) and before Japan (2,000 mt Ag in 1978). Table 5.1.a. shows the breakdown of silver demand by uses in the EEC countries.

The 1985 forecast of the EEC silver consumption is based on the analysis of the possible developments of silver demand by uses in the EEC countries and is rated at 4,530 mt Ag, (cfr. table 5.1.b.).

Table 5.1.a. 1978 SILVER CONSUMPTION IN EEC COUNTRIES

| End-uses | E E C |  | Belgium |  | France |  | W.Germany |  | Italy |  | United Kingdon |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | mtAg | % | mtAg | % | mtAg | % | mtAg | % | mtAg | % | mtAg | % |
| Photo industry | 1588 | 41 | 558 | 90 | 248 | 36 | 213 | 26 | 162 | 20 | 407 | 45 |
| Elec-Electronic industry | 587 | 15 | 6 | 1 | 138 | 20 | 131 | 16 | 105 | 13 | 207 | 23 |
| .contacts and electronic components | n.a. |  | n.a. |  | 123 |  | n.a. |  | 105 |  | 167 |  |
| .batteries | n.a. |  | n.a. |  | 15 |  | n.a. |  | - |  | 40 |  |
| Brazing alloys & soldering | 496 | 13 | 25 | 4 | 117 | 17 | 90 | 11 | 129 | 16 | 135 | 15 |
| Jewelry and Silverware | 800 | 20 | - | - | 180 | 26 | 205 | 25 | 388 | 48 | 27 | 3 |
| Other industrial uses | 429 | 11 | 31 | 5 | 7 | 1 | 182 | 22 | 25 | 3 | 126 | 14 |
| Total industrial uses | 3900 |  | 620 | 100 | 690 | 100 | 821 | 100 | 809 | 100 | 902 | 100 |
| Coinage | 457 |  | - |  | 345 |  | 112 |  | - |  | - |  |
| Total consumption | 4357 |  | 620 |  | 1035 |  | 933 |  | 809 |  | 902 |  |

| Table 5.1.b. | THE 1985 OUTLOOK FOR SILVER CONSUMPTION IN THE EEC (mt Ag-yearly growth from 1978) | | | | | |
|---|---|---|---|---|---|---|
| End-uses | E E C | Belgium | France | W.Germany | Italy | United Kingdom |
| **Photo-industry** | 1690 +0.9% | 590 +0.8% | 300 +2.8% | 230 +1.1% | 170 +0.7% | 400 -0.2% |
| **Elec-Electronic industry** | 600 +0.3% | 5 -2.6% | 135 -0.3% | 140 +1.0% | 90 -2.2% | 230 +1.5% |
| **Brazing alloys & soldering** | 500 +0.1% | 25 0% | 120 +0.4% | 90 0% | 130 +0.1% | 135 0% |
| **Jewelry & Silverware** | 825 +0.4% | | 180 0% | 205 0% | 390 0% | 50 0% |
| **Other industrial uses** | 565 +4.0% | 35 +1.7% | 30 +23% | 235 +3.7% | 35 +2.6% | 160 3.5% |
| **Total industrial uses** | 4180 +1.0% | 655 +0.8% | 765 +1.5% | 900 +1.3% | 815 +0.1% | 975 +1.1% |
| **Coinage** | 350 | | | | | |
| **Total consumption** | 4530 +0.6% | | | | | |

The bulk of the silver supply to the EEC industry consists of imported material, whether they are base metal products containing silver (Cu, Pb, Zn concentrates, blister..) or unwrought silver and silver alloys. Silver supply generated within the EEC countries consists only of about 200 t Ag from mine production and an estimated 700 to 800 t Ag from industrial scrap.

Nothing allows to assume that this situation of dependence on foreign silver sources might change drastically in the future.

The status of silver as an investment commodity gained importance over the 70's with the generalization of inflation and the growing confusion of the international monetary system. These factors induced investors and speculators to turn to silver as second hedge commodity after gold, and speculative demand plays now a determinant role in price fluctuations, superseding in the short term the supply/demand effects linked to the industrial activity. Speculation should bring the 1979 average price at an all-time high of 500 pence/ounce (282 pence/ounce in 1978) Five hundred pence/ounce might be considered as a new "price plateau" resulting from the integration into the price structure of the now clearly evidenced status of silver as an investment commodity, and future prices should develop starting from this level.

Over the long term, the price of silver will be growing in accordance with the long-lasting imbalance of the market, primary supply showing an irremediable deficit towards total needs.

The price of silver ought to keep rising in the foreseeable future since the primary production deficit will subsist and the release and reclaiming of the required above-ground resources will imply price increases in line with cost inflation.

It is therefore suggested that the silver price should fluctuate around 700 pence/ounce by 1985, with possible large variations from this trend value, linked to speculative activity or temporary sharp imbalances in the supply/demand relationship for industrial use.

## 5.2. Recommendations for research and development

Complete or partial substitution of other materials for silver should be feasible in some industrial applications. The substitution process could develop spontaneously or through a deliberate action from the silver consumers, it should also be encouraged outside the industry whenever the required R&D effort could not be initiated or pursued by individual users. The implementation of substitutes will be progressive and must be viewed as a long-lasting process with the most significant impact to be felt after the mid-eighties if R&D is undertaken right now.

The most promising R&D orientations for substitution arise in the three major silver consuming sectors :

- photography (sensitive surfaces);
- electricity and electronics (contact materials);
- engineering industry (brazing alloys).

The selected R&D themes are summarized hereafter with reference to the motivations prompting to adopt each one of them, the benefit to be expected from a substitution policy, the required financing, the possible location of the R&D action. It results from the present study that a significant R&D programme for substitution in the European Economic Community

| Field where R&D action should be undertaken | Present share in EEC silver market (%) | EEC financing support needed for R&D ( M.U.C. for 5 years ) | Annual growth rate (%) assuming |  | Industrial vulnerability if supplies unavailable | R&D themes | Priority to be given |
|---|---|---|---|---|---|---|---|
|  |  |  | Preservation policy | Substitution policy |  |  |  |
| Photography | 41 | 0.5 | + 0.9 (1)<br>+ 1 (2) | + 0.7 (1)<br>0 (2) | xx | Improvement of silver efficiency in silver surfaces. | ++ |
|  |  |  |  |  | xx | Research connected with non-silver photosensitive materials. | ++ |
|  |  |  |  |  | xx | Improvement of already existing non-silver photosensitive materials (quantum efficiency, definition,...). | + |
|  |  |  |  |  | 0 | Improvement of the technical characteristics of photopolymer films used in printing paper. | + |
| Electrical contacts | 15 | 2.5 | + 0.3 (1)<br>+ 0.2 (2) | - 0.2 (1)<br>0 (2) | xxx | Substitution of more common materials for silver in the contacts field. | ++ |
|  |  |  |  |  | xxx | Study of the role of filler elements such as CdO on the properties of contacts. | ++ |
|  |  |  |  |  | xxx | Study of the way of impairment of silver-base contact materials (under arc effect). | ++ |
|  |  |  |  |  | xxx | Research and development as to new silver contact manufacturing technologies saving more precious metal (powder and other techn.). | ++ |
|  |  |  |  |  | xxx | Study on hardening of contact materials by appropriate treatment. | ++ |
| Brazing alloys | 13 | 2.0 | + 0.1 (1)<br>0 (2) | - 1.4 (1)<br>- 2 (2) | x | New mode of assembling metals requiring no brazing. |  |
|  |  |  |  |  | x | Development of automatic brazing processes and pastes that can be used with this technology. | ++ |
|  |  |  |  |  | x | New materials substituting for metals and doing without brazing. | + |

KEY :
x = slight.
xx = considerable.
xxx = very considerable.

(1) = 1978-1985.
(2) = 1985-1990.

++ = priority study.
\+ = non-priority study.

would require 5.5 M.U.C. for 5 years; the breakdown of such a budget by consuming sector would preferably be as follows :

1.0 M.U.C. for photography (i.e. 18.1 % of the total budget);
2.5 M.U.C. for electrical contacts (i.e. 45.5 % of the total budget);
2.0 M.U.C. for brazing alloys (i.e. 36.4 % of the total budget).

The above distribution of the budget takes into account the fact that the photography industry is currently the most advanced and best organized one in the field of Ag substitution research as compared with the electrical-electronic industry and the brazing-soldering sector. However, it should be stressed that 1 M.U.C. poorly compares with the large sums already spent and still currently allocated by the photography industry for Ag substitution research programmes.

### 5.2.1. Photography industry

#### Incentives to substitution

- The photography industry is rather vulnerable to supply disruption or price surge, since
  - . it absorbs 41 % of the total silver consumed by the industrial sector in the EEC and 90 % of the sensitive surfaces produced require the use of silver; furthermore, more than half of the silver-bearing sensitive surfaces are consumed by the health services and the industrial research laboratories;
  - . exceptional silver price rises cannot easily be passed on to the finished product prices which are tied to marketing policy and price lists; significant silver price increases have therefore a sharp impact on the companies' cash flow since silver represents 10 to 25 % of the production costs in this sector.
- The photography industry employs about 50,000 people in the EEC and, in 1977, its production represented a turnover of 2,074 million Dollars (sales price to wholesalers).

### Silver demand evolution and impact of a substitution policy

Research efforts undertaken by the photography industry itself have already achieved significant results, i.e. a reduction of 2 to 3 % per year in the specific consumption of silver, inducing a stabilization of the total silver demand although the production of sensitive surfaces follows a growing trend. Currently ongoing research in the industry should still improve the efficiency of silver use and limit the total silver demand growth to 0.9 % per year until 1985. Thereafter, two factors should influence silver demand from the photography industry beside the growth of the industry itself :

- the reaching of a treshold as far as minimum specific consumption of silver is concerned should allow the full impact of the sector growth on silver demand;
- the generalization of totally different processes such as video, electronic recording in radiography..., none requiring silver, should reduce silver needs of the industry.

These two counteracting tendencies should result in a 1 %/year growth rate of the silver demand from the photography industry during the period 1985-1990.

### Financing required

The photography industry already spent millions of Dollars to reduce its dependence on silver and research programmes are undoubtedly still being conducted by the large companies. Considering the limitations of the total budget to be allocated to the various Ag-consuming industries and the importance of the research effort already made by the photography industry itself, it seems reasonable to allocate 1 M.U.C. during five years for very specific research themes.

## R&D themes

### Applied research

a. Improvement of silver efficiency in sensitive surfaces.
It seems possible to further reduce the specific consumption of silver in sensitive surfaces :

- by improving the quantum efficiency of emulsions through the introduction of more effective sensitizers;
- by reducing the thickness of the emulsions;
- by reducing flaws and fabrication scrap.

Development studies are carried on in the industry research laboratories which are most appropriate to perform this type of work. Nevertheless, a financial aid from the EEC could possibly help obtain results more rapidly.

b. Improvement of existing non-silver sensitive materials.
It seems possible to increase the photomultiplier capacity, the definition and resolution capacity of existing non-silver photosensitive materials such as diazos, photopolymers and dichromic resins; the use of such materials could then be extended to the prejudice of silver salts; these materials are successful competitors to silver in the copying of documents and maps and are making some inroads in graphic arts and microfilming although silver remains the preferred material in the latter applications.
R&D should be limited in time and resources, because its net impact would probably be limited since it is unlikely that non-silver sensitive materials will ever represent a majority share of the silver salts market.

### Fundamental research

c. Research into non-silver photosensitive materials.
Silver salts are presently the most light-sensitive materials to exist, they undergo continuous technical evolution which, day after day, enlarges their fields of application; non-silver photosensitive materials must offset their lower sensitivity to light by longer exposure time and this limits

their use to some applications only, for instance : diazos are used to reproduce drawings and microfilms with a limited resolution capacity, photopolymers and dichromic resins may be used in graphic arts.
It seems, however, that new photosensitive materials could be discovered and could substitute for silver salts in black and white photography, instant or not. Similar research is of lesser necessity in colour photography, since all the silver used in this field can be recovered in the development baths. Such research would require a lot of time and finance, and its results are hypothetical.

### Development

d. Improvement of the technical characteristics of films and photopolymers used in printing paper.
The present quality of films and photopolymer based printing paper limits their use to the graphic arts, whence several lines of R&D :

- . increase in the mechanical strength offering a larger number of prints and higher speed;
- . reduction in the wear of the photopolymer or the subjacent layer; so as to avoid impairment of the picture;
- . improvement of the adherence of the photopolymer to the sublayer.

However, the substitution of these improved materials will be of minor significance only to the silver market.

### Location of R&D

The photography industry is well equipped to carry out R&D work aiming at improving existing products and at developing new ones. EEC financial help should preferably reinforce the ongoing and future R&D programmes conducted within the industry.

### 5.2.2. Electrical-electronic industry

#### Incentives to substitution

- The elec.-electronic industry in the EEC absorbs 15 % of the total silver demand and is growing at a relatively fast rate of 5 % per year since 1975.
- The silver share in the cost price of unequipped finished contacts may reach 70 to 80 % in the case of low voltage contacts (Ag-CdO and Ag-Ni) and, more generally, 50 %; it is, however, considerably lower in relays and switches (more or less 0.25 %)

#### Silver demand evolution and impact of a substitution policy

The silver demand from the elec.-electronic industry varied very little during a number of years, the growth of the sector being offset by the use of techniques requiring less and less silver.
Further silver savings should be expected in the future owing to :

. giving up the use of electromechanical switching in telephony;
. the development of miniaturization and solid-state microtechnology in electronics, which should imply the disappearance of mechanical contacts and a more extensive use of platinum or palladium;
. the extension of the contacts life time;
. the development of new manufacturing processes for contacts.

In other contact applications, silver demand ought to grow together with the growth of the sector.
Up to 1985, the overall growth of the silver demand from the elec.-electronic industry should be little affected by a substitution policy, the impact of which should be more sensible during the second half of the 80's.

### Financing required

Potential outcomes of a substitution policy in the sector as well as a lesser centralization of research efforts than in the case of the photography industry, would justify an EEC financial support of 2.5 M.U.C.

### R&D themes

Applied research

e. Study of the mode of impairment of silver based contact materials under the arc effect.
Such research should lead to a better adequacy of contacts to the stresses they are subjected to, hence it would increase the service life of the products; in fact, in the sector of contacts, many phenomena are poorly explained or understood and empirism too often guides the choice of the materials to be used in such or such conditions; research in this field would certainly improve the efficiency and the working life of the products; it is currently carried out in many centres and laboratories throughout the world and would justify an EEC support, as it could result in a reduction of the silver requirements.
The above research could be undertaken as part of a university programme and should bear results by 1985.

f. Research and development of new technologies for the manufacture of contacts.
A reduction of the specific silver consumption in contacts has already been achieved for a particular type of contacts through the use of improved technologies which developed in four stages :

- plain rivets in pure or alloyed silver;
- bi- or trimetal rivets (Ag-Cu or Ag-Cu-Al), silver being plated on a support most often made of copper;
- solid silver button soldered to the blade and no longer riveted;
- bimetal button obtained by sintering powder technology, soldered to the blade.

The fourth technique leads to a substantial (70 %) saving of silver when compared with the first one, but the higher production cost involved and special equipment requirements preclude its generalization to already existing production lines, so that the first three techniques are still currently applied.

In this respect, a first research theme would be to develop the knowledge and application of sintering powder metallurgy in the field of electrical contacts, and a further research theme would be the analysis of the silver deposition process on a support made of a common metal; such research could possibly be extended to the investigation of techniques other than galvanoplasty.

The above research lines could lead to silver savings in the new products as from 1985.

### Fundamental research

g. Substitution of common metals for silver in contacts.

This is a very important though rather difficult line of research which may have a significant impact in the long term at an industrial level; cuprous products, lead-tin alloys appropriately treated may be of interest; this list is far from being exhaustive although attention should be drawn only to those metals which would not be affected by supply problems similar to those encountered by silver; it is very likely that the alternative materials will have narrow fields of application and will require larger specialization not only of the contacts but also of the equipment; even further, they could require the development of new technologies.

The above research could last more than three years and, if successful, appreciable results should not be expected until the end of the 80's.

h. Role of filler elements on contact properties.

Cadmium oxide, tungsten, tungsten carbide should be tested as well as new addition elements such as refractory materials; the ultimate objective of the research should be to reduce silver consumption by increasing the share of addition elements in contacts; the study might possibly lead to the replacement of the Ag-CdO alloy used in high voltage contacts which is polluting; significant results could be reached as early as in 1985.

Development

i. Hardening of contact materials.
Improved manufacturing processes and contact treatments could confer greater hardness and better friction characteristics on electrical contacts, thus extending the life time of the finished products; such research could lead to interesting results within a relatively short period of time and, hence, contribute to a reduction of the silver demand by 1985.

Location of R&D

Professional and independent research centres seem to be in a better position to undertake R&D in the sector than contact manufacturers who are often integrated or closely linked to silver refiners. University research units should be interested in such research programmes.

### 5.2.3. Brazing and soldering

Incentives to substitution

Brazing and soldering create 13 % of the total silver demand in the EEC.
Many industrial sectors are using silver brazing : the consumer goods industries, the engineering industry, the transportation industries, the building industry; nevertheless, for certain types of finished pproducts, several alternatives to silver brazing do exist, so that the sector is less vulnerable than the electricity and photography sectors; furthermore, the share of silver in the cost price of the finished product is usually very low, even less than 1 %.

### Silver demand evolution and impact of a substitution policy

Despite the growth of industrial production, silver demand for brazing alloys increased very little in the past and it should be expected to keep on stagnating in the future. Several factors account for such a situation :

- the reduction of the silver content of most of the brazing alloys, from 40 to 30 % on an average, which is linked largely to the improvement of brazing techniques;
- the generalization of the use of preforms having the shape of the part to be brazed, thus reducing the application losses;
- the generalization of brazing machines which allow to better determine the quantity of alloy and to use alloys containing less silver.

Reduction in the silver demand for brazing might be expected in the future if automatic brazing processes did generalize and if new assembly technologies requiring no brazing, were developed. The latter development would in fact imply substitution at the level of the construction materials to be assembled. The impact of the above developments on silver consumption should, however, not be significant until 1985.

### Financing required

R&D in the field of brazing could easily require a financial support of 2 M.U.C. for five years.

### R&D themes

Applied research

- New assembly processes requiring no brazing.

Silver brazing is often required in the assembly of metal pieces because of the special properties silver gives to the brazing alloy, i.e. increased resistance to corrosion, increased tensile strength, high electrical conductivity. Silver is thus alloyed to Cu, Zn, Sn or Cd in variable proportions which may exceed 50 %. An immediate way of reducing silver demand for brazing would be to investigate new assembly processes such as bonding or friction assembly, so as to eliminate the brazing operation; some results could be achieved in this field by 1985.

- New materials to substitute for metals and which would not require brazing for their assembly.
  The use of new materials, such as polymers, should be promoted in the automobile and buidling industries so as to reduce the silver brazing operations thus replaced by other assembly processes. Such research would be rather important since it requires a new concept of the final products and would imply rather fundamental changes at various manufacturing levels. Its impact on silver demand should, therefore, not be expected until 1990.

Development research

- Development of automatic brazing processes and of the required brazing pastes.
  Automatic brazing of batch parts is performed with precision machine tools and brazing pastes instead of wires and beads; automatic brazing allows substantial savings at various levels since :
  . it reduces specific brazing consumption by 20 % or more through the deposition of the brazing on those points only where required;
  . it allows the use of lower silver containing alloys, as temperature can be set more accurately or raised to higher levels;
  . it is half less energy consuming than conventional brazing processes because the surface to be worked is reduced and acetylene may replace propane in some machines;
  . it allows to reach higher production rates.

The development of automatic brazing processes requires the simultaneous development of a range of brazing pastes and fluxes with different characteristics and Ag content.

Automatic processes have already been developed by several companies, either producers or consumers; their use is recent, not very widespread and still involves numerous technical problems which should be solved. Moreover, the development of a machine adapted to each case seems to be necessary.

Automatic brazing processes could induce substantial silver savings in the brazing sector before 1985 if their use is encouraged by appropriate advertising and further perfecting of the techniques.

### R&D location

The brazing manufacturers -mainly the refiners- do not seem to be in the best position to undertake this work and, at any rate, would not be looking for any outside help.

EEC financial support should preferably be directed to the users of brazing alloys, mainly the automobile industry which might be interested in the development of new assembly methods for metal parts or the investigation of new materials requiring no brazing. Smaller industries could undertake a survey of the automatic brazing processes with the help of the large brazing users (automobile and electricity industries). Specialized organizations, such as the Istituto di Ricerche Breda in Italy, should also be approached to carry out a research programme on the replacement of Ag brazing by other brazing materials or other brazing techniques.

## 5.3. Silver economies resulting from substitution efforts

Starting from the 1978 breakdown of silver consumption in the EEC countries, two cases are proposed for the 1985-1990 silver demand :

- case A assumes that no particular research effort aiming at silver replacement is undertaken and that currently ongoing technological changes will come to completion in each of the major end-use sectors; case A implies the following yearly growth rates per use (%) :

| | over the period | |
|---|---|---|
| | 1979-1985 | 1986-1990 |
| photo industry | + 0.9 | + 1.0 |
| elec-electronic industry | + 0.3 | + 0.2 |
| brazing and soldering | + 0.1 | 0 |
| jewelry and silverware | 0 | 0 |
| other industrial uses | 4.0 | 5.0 |
| Total industrial consumption | 1.0 | 1.1 |

Changes in annual growth rates are linked to the time pattern of technological progress, for instance solar energy systems are supposed to be developed largely during the second half of the 80's inducing a stronger growth of silver demand for "other industrial uses", while technological progress in the electronic industry and in brazing and soldering will extend their "shrinking" influence on silver demand well after the mid 80's.

- case B assumes that willful research and development efforts are undertaken right now to lower the use of silver wherever possible, either through replacement by other materials or other processes, or through improved efficiency in the use of the precious metal; such a "substitution policy" aiming at silver economies would be fruitful in the long term, since the implied research and development process is time consuming, and it is likely that the impact of such a policy would be noticeable mainly as from the mid 80's; the growth rates by uses implied by case B are as follows :

| | over the period | |
|---|---|---|
| | 1979-1985 | 1986-1990 |
| photo industry | 0.7 | 0 |
| elec-electronic industry | - 0.2 | 0 |
| brazing and soldering | - 1.4 | - 2.0 |
| jewelry and silverware | 0 | 0 |
| other industrial uses | 4.0 | 5.0 |
| Total industrial consumption | 0.7 | 0.5 |

The above table emphasizes that three major consuming sectors should be affected by R&D developments : the photo industry, the electrical and electronic industry and the brazing alloys.

Table 5.3.a. compares 1978, 1985 and 1990 silver consumption in the EEC countries, in both cases A and B. It should be noted that the various assumptions do not imply a major drift in the breakdown of silver demand by uses.

If R&D is undertaken, the total silver economies realized by 1985 might amount to 170 mt Ag considering that no gain in silver demand could be expected before 1983 because of the time required to implement the first R&D results; about 20 % of the gains could be realized in 1983, a further 30 % in 1984 and 50 % in 1985.

Valued at the estimated 1979 average price of £ 5 per ounce, these silver economies would represent about 27 million £.

Much more substantial silver economies could be achieved over the period 1986-1990, i.e. around 855 mt Ag over the five-year period. Valued at the estimated 1985 average price of £ 7 per ounce, these silver economies would represent 192 million £.

It should be emphasized that 170 mt Ag represent less than 1 % of the total EEC silver needs over the period 1979-85, but the 855 mt Ag saved over the period 1986-1990 could represent almost 4 % of the total EEC needs during the second half of the 80's.

Considering that silver economies deriving from substitution are to be regarded as a long-term objective, it would be interesting to contemplate alternative ways of reducing the risks of silver supply disruption or inadequacy in the short term. In this respect, the improvement of silver

Table 5.3.a. - Silver industrial consumption in the EEC countries by 1985-1990

| End-uses | 1978 | | 1985 | | | | 1990 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | case A | | case B | | case A | | case B | |
| | mt Ag | % | mt Ag | % | mt Ag | % | mt Ag | % | mt Ag | % |
| Photography industry | 1,588 | 41 | 1,690 | 40 | 1,670 | 41 | 1,775 | 40 | 1,670 | 40 |
| Elec-electronic industry | 587 | 15 | 600 | 14 | 580 | 14 | 605 | 14 | 580 | 14 |
| Brazing alloys and soldering | 496 | 13 | 500 | 12 | 450 | 11 | 500 | 11 | 405 | 9 |
| Jewelry and silverware | 800 | 20 | 825 | 20 | 825 | 20 | 825 | 19 | 825 | 20 |
| Other industrial uses | 429 | 11 | 565 | 14 | 565 | 14 | 720 | 16 | 720 | 17 |
| Total industrial consumption : | 3,900 | 100 | 4,180 | 100 | 4,090 | 100 | 4,425 | 100 | 4,200 | 100 |
| Yearly growth rate of the total industrial consumption : | | | 78-85: 1.0% | | 78-85: 0.7% | | 85-90: 1.1% | | 85-90: 0.5% | |

recycling should be actively promoted. It is much more a matter of organization and logistics than a matter of processing. In the photography sector, for instance, silver recycling should be organized so as to allow the circulation of the precious metal in closed circuit; this would imply systematic reclaiming of silver-bearing photo products from the private as well as from the producing and consuming industries. Recycling of the elec-electronic products could be intensified provided an economically feasible organization for the collection, dismantling and processing of that kind of scrap could be set up.

Increased recycling would obviously require additional scrap processing units, the location of which should be studied in relation with the scrap market itself so as to minimize some basic costs such as transportation costs.

## Ag RECOVERY METHODS APPLIED TO PHOTOGRAPHY SCRAP MATERIALS

There are basically three kinds of scrap generated by the photography industry :

- photography wastes at the manufacturing stage;
- developed films and papers;
- used developer solutions.

The nature of the photography scrap material determines the recovery method to be used for silver recycling

1. Solid scrap treatment (mainly photography wastes and medical and industrial X-ray plates).
   There are basically two kinds of treatment according to the nature of the support :
   a/ scrap containing cellulose triacetate (amateur films and professional cinema) are treated through
      - washing;
      - drying, burning and melting of the resulting slimes;
      - recycling of the triacetate and Ag recovery.

      The recovery rate of Ag varies according to the Ag content of the scrap processed, there is a loss of 2 to 3 % Ag in fumes when burning.

   b/ scrap containing polyester (medical and industrial X-ray plates, surfaces for graphic arts, films, professional photography and portraits), can be treated following two different routes :
      i) washing, methanolysis yielding dimethylterephthalate, and recycling of the polyester together with the Ag recovery,
         or
      ii) burning with subsequent melting of the resulting ash and dust fumes to allow Ag recovery.

The first method is common practice in the U.S A. where tonnages to be recycled are important and justify the recovery of polyester, whereas the second route is used in Europe, where the recovery of polyester is not economical; both processes imply some recovery losses which could be reduced by the implementation of fume washers at the burning and smelting units; the average Ag content of the polyester-containing scrap varies between 1.2 and 1.35 % of product weight.

The treatment of solid scrap materials from the photo industry in the EEC countries is handled mainly by the following companies :

| | | |
|---|---|---|
| . in France, | Kodak-Pathé | burning unit for polyester-base scrap, 2200 t/year capacity; presently running at 100 % capacity. |
| | CLAL | treatment units for both polyester-base and cellulose triacetate-base scrap; presently expanding capacity. |
| | Berger<br>Cometa | ( less important.<br>( |
| . in Germany, | Degussa | |
| . in Italy, | Engelhard | |
| | Metalli Preziosi | |
| | Zucchini (Chimet) | |
| . in the U.K., | Johnson Matthey Chemicals | |
| | John Bates Refiners | |
| | Lucas | |
| | Engelhard | |
| . in Belgium, | Etma | |
| | MHO | |
| | Gevaert | |

2. Liquid scrap treatment (used developer solutions, waste waters).

Two main routes are available to recover silver contained in liquid scrap :

a/ the electrolytic process without recirculation :
it achieves a 70 to 80 % recovery rate and the solution is lost;

b/ the electrolytic process with recirculation :
it achieves a 95 % recovery rate and allows the recycling of part of the solution; the recycled silver contains minimum 90 % Ag.

30 % of the liquid scrap is recycled through this latter route in the U.S.A., while the classical route without recirculation is still largely prevalent in Europe.

The use of both processes is made possible through the installation by the users (hospitals, laboratories, printers) of appropriate equipments which are supplied and maintained by the silver recycling companies.
Such equipments are distributed in Europe by :

CLAL (2700 machines)
TBP (500 machines)
Martineau (700 to 800 machines)
Sica-Worms in France.

Fotomec
Filmchimica e Eurochimica
Chimifoto Ornano
Arfo e Dara
Fusarg
Sofai in Italy.

Photographic Silver Recovering Ltd.
Ilford in the U K.

Gevaert in Belgium.

The four different routes pf scrap treatment presented above are not the only existing ones. Many other processes do exist, most of them being however variants of a few basic processes.

APPENDIX 2

## IMPORTS OF SILVER AND ITS ALLOYS,UNWROUGHT, IN THE EEC COUNTRIES

- items 71.05.010 - 71.05.030 of the Brussels Nomenclature
  681.11 - 681.13 of the SITC Nomenclature

- mt Ag

### FRANCE IMPORTS

| from | 75 | 76 | 77 | 78 |
|---|---|---|---|---|
| EEC | 192 | 789 | 660 | 562 |
| of which | | | | |
| Belgium | 35 | 81 | 57 | 103 |
| W.Germany | 6 | 30 | 15 | 27 |
| Netherlands | 36 | 38 | 66 | 39 |
| United Kingdom | 115 | 640 | 522 | 391 |
| INDIA | 299 | 183 | 446 | 230 |
| POLAND | 8 | 58 | 26 | 30 |
| MEXICO | 93 | 75 | 75 | 95 |
| SWEDEN | 39 | 27 | 59 | 32 |
| SWITZERLAND | 37 | 116 | 49 | 49 |
| OTHER COUNTRIES | 239 | 33 | 61 | 132 |
| TOTAL | 907 | 1281 | 1376 | 1130 |

IMPORTS OF SILVER AND ITS ALLOYS,UNWROUGHT,IN THE EEC COUNTRIES

- items 71.05.010 - 71.05.030 of the Brussels Nomenclature
  681.11 - 681.13 of the SITC Nomenclature
- mt Ag

WEST GERMANY IMPORTS

| from | 75 | 76 | 77 | 78 |
|---|---|---|---|---|
| EEC | 301 | 498 | 579 | 396 |
| of which | | | | |
| Belgium | 190 | 188 | 135 | 99 |
| France | 7 | 102 | 50 | 31 |
| Netherlands | 21 | 38 | 66 | 38 |
| United Kingdom | 81 | 167 | 328 | 228 |
| SWEDEN | 138 | 104 | 131 | 131 |
| SWITZERLAND | 60 | 88 | 98 | 221 |
| POLAND | 54 | 100 | 98 | 119 |
| U.S.A. | 60 | 139 | 448 | 94 |
| MEXICO | 27 | 2 | - | 4 |
| NORTH KOREA | 93 | 67 | 33 | 56 |
| INDIA | 5 | 144 | 22 | 15 |
| YOUGOSLAVIA | 46 | 28 | 28 | 25 |
| CHILE | 79 | 27 | 30 | 43 |
| PERU | - | - | 29 | 44 |
| CANADA | - | - | - | 67 |
| TOTAL | 934 | 1238 | 1581 | 1292 |

## IMPORTS OF SILVER AND ITS ALLOYS,UNWROUGHT,IN THE EEC COUNTRIES

- items 71.05.010 - 71.05.030 of the Brussels Nomenclature
  681.11 - 681.13 of the SITC Nomenclature

- mt Ag

### ITALY IMPORTS

| from | 75 | 76 | 77 | 78 |
|---|---|---|---|---|
| EEC | 304 | 374 | 290 | 369 |
| of which | | | | |
| Belgium | 111 | 116 | 94 | 56 |
| West Germany | 60 | 64 | 42 | 123 |
| United Kingdom | 128 | 190 | 154 | 190 |
| INDIA | 53 | 20 | 3 | n.a. |
| POLAND | - | 40 | 61 | 54 |
| MEXICO | 26 | 19 | 40 | n.a. |
| U.S.A. | 233 | 318 | 352 | 292 |
| SWITZERLAND | 33 | 5 | 21 | n.a. |
| OTHER COUNTRIES | - | - | - | 40 |
| TOTAL | 730 | 804 | 775 | 755 |

## IMPORTS OF SILVER AND ITS ALLOYS,UNWROUGHT,IN THE EEC COUNTRIES

- items 71.05.010 - 71.05.030 of the Brussels Nomenclature
  681.11 - 681.13 of the SITC Nomenclature

- mt Ag

### NETHERLANDS IMPORT

| from | 75 | 76 | 77 | 78 |
|---|---|---|---|---|
| EEC | 63 | 340 | 113 | 112 |
| of which | | | | |
| Belgium | - | - | 16.5 | 33 |
| West Germany | 30 | 12.3 | 4.3 | 6 |
| France | 17.4 | 4.1 | 50 | 18 |
| United Kingdom | 11.7 | 321.7 | 39.9 | 52 |
| Denmark | 1.2 | 2.3 | 2.9 | 2 |
| Italy | 2.9 | - | - | - |
| SWITZERLAND | 14.5 | 12.7 | 17.3 | 5 |
| POLAND | 11 | 5.1 | - | - |
| U.S.A. | 21 | - | - | - |
| MEXICO | 15.1 | - | - | - |
| TOTAL | 125.3 | 359.4 | 133.0 | 118 |

IMPORTS OF SILVER AND ITS ALLOYS,UNWROUGHT, IN THE EEC COUNTRIES

- items 71.05.010 - 71.05.030 of the Brussels Nomenclature
  681.11 - 681.13 of the SITC Nomenclature

- mt Ag

UNITED KINGDOM IMPORTS

| from | 75 | 76 | 77 | 78 |
|---|---|---|---|---|
| EEC | 556 | 169 | 150 | 136 |
| of which | | | | |
| Belgium | 144 | 113 | - | - |
| West Germany | 106 | 43 | 55 | - |
| France | 233 | - | 69 | 127 |
| Italy | 7 | - | - | - |
| SWITZERLAND | 17 | - | - | - |
| EAST GERMANY | 63 | 112 | 270 | 218 |
| SOUTH AFRICA | 62 | 60 | 62 | 68 |
| INDIA | 890 | 890 | 159 | 349 |
| AUSTRALIAN | 69 | 68 | 83 | 106 |
| U.S.A. | 636 | 73 | 117 | 84 |
| MEXICO | n.a. | 85 | 209 | 171 |
| TOTAL | 2540 | 1560 | 1119 | 1306 |

## RAW SILVER EXPORTS (°) OF THE EEC COUNTRIES IN 1977

(mt Ag)

| Exports to / from | Germany | Belgium | France | Great (°°) Britain | Italy | The Netherlands |
|---|---|---|---|---|---|---|
| Germany | --- | 131,5 | 46,3 | 240,- | negligible | 68,4 |
| Belgium | 29,2 | --- | - | - | | 78,3 |
| France | 18,3 | 56,5 | --- | 525,- | | 47,4 |
| Great-Britain | 1,0 | 331,6 | 49,2 | --- | | 18,0 |
| Italy | 56,2 | 86,2 | 15,0 | 174,- | | - |
| The Netherlands | 4,3 | 35,2 | 38,6 | 50,- | | --- |
| Other EEC | 3,0 | - | 0,2 | 56,- | | 0,3 |
| Other countries | 175,6 | 52,2 | 561,8 | 604,- | | 23,7 |
| Total EEC | 112,0<br>39 % | 641,1<br>92,5 % | 149,3<br>21 % | 1.045,-<br>63 % | | 212,3<br>90 % |
| Grand total | 287,6 | 693,3 | 711,1 | 1.649,- | | 236,0 |

---

(°) Items 71.05.010 - 71.05.030 of the Brussels Nomenclature.

(°°) Item 681.11 of the SITC Nomenclature

Appendix 3
(continued)

## RAW SILVER IMPORTS (°) OF THE EEC COUNTRIES IN 1977

(mt Ag)

| Imports in / from | Germany | Belgium | France | Great-Britain | Italy | The Netherlands | Other EEC | Other countries | Total EEC | Grand total |
|---|---|---|---|---|---|---|---|---|---|---|
| Germany | --- | 135,6 | 49,3 | 327,7 | - | 65,9 | 0,7 | 1002,0 | 579,2<br>37% | 1.581,2 |
| Belgium | 23,5 | --- | 0,1 | 82,6 | - | 365,6 | - | 712,3 | 471,8<br>40% | 1.184,1 |
| France | 15,2 | 56,5 | --- | 521,6 | - | 65,6 | 0,6 | 716,3 | 659,5<br>48% | 1.375,8 |
| Great-Britain (°°) | 55,0 | n.a. | 69,0 | --- | - | n.a. | 26,0 | 969,0 | 150,0<br>13% | 1.119,0 |
| Italy | 42,1 | 94,3 | - | 153,5 | --- | 0,5 | - | 484,9 | 290,4<br>37% | 775,3 |
| The Netherlands | 4,3 | 16,5 | 50,0 | 39,9 | - | --- | 2,9 | 19,9 | 113,5<br>85% | 133,4 |
| Other EEC | | | | | | | | | | |

(°) Items 71.05.01 and 71.05.03 of the Brussels Nomenclature.

(°°) Item 681.11 of the international SITC Nomenclature.

# Typical properties of light duty contact materials

**TARNISH-FREE MATERIALS**

| MATERIAL | | Specific Gravity | Hardness (Annealed), HV | Melting Point (Solidus), °C | Specific Resistance, µΩ cm | Electrical Conductivity, %IACS | Thermal Conductivity, Approximate W/mK |
|---|---|---|---|---|---|---|---|
| **PLATINUM** | Platinum* | 21.3 | 65<br>400** | 1768 | 11.6 | 15 | 70 |
| | 10% iridium-platinum | 21.6 | 120 | 1780 | 24.5 | 7.0 | 310 |
| | 20% iridium-platinum | 21.7 | 200 | 1815 | 30.0 | 5.7 | 175 |
| | 25% iridium-platinum | 21.7 | 240 | 1845 | 32.0 | 5.4 | 165 |
| | Iridium-ruthenium-platinum (Irru) | 20.8 | 310 | 1890 | 39.0 | 4.4 | † |
| **RHODIUM** | Rhodium | 12.4 | 800** | 1960 | 4.9 | 35 | 150 |
| **PALLADIUM** | Palladium | 12.0 | 40<br>350** | 1552 | 10.7 | 16 | 75 |
| | 40% silver-palladium | 11.0 | 95 | 1290 | 43.0 | 4.0 | 30 |
| | 40% copper-palladium | 10.4 | 145 | 1200 | 35.0 | 4.9 | † |
| | JMM 77 Alloy | 12.0 | 210†† | 1085 | 37.5†† | 4.6†† | † |
| **GOLD** | Fine gold | 19.3 | 60** | 1064 | 2.4 | 68 | 290 |
| | JMM hard gold | 19.1 | 115** | 1057 | 2.4 | 68 | 290 |
| | 5% nickel-gold | 18.3 | 100 | 998 | 14.1 | 12 | † |
| **COPPER-SILVER-GOLD** | JMM 625 Alloy | 13.7 | 160-190*** | 861 | 14.0 | 12 | † |
| | JMM 625R Alloy | 14.4 | 95 | 1014 | 12.5 | 14 | † |
| | 30% silver-gold | 16.6 | 32 | 1025 | 10.4 | 16 | 65 |
| | Platinum-silver-gold (PGS Alloy) | 17.1 | 60 | 1100 | 16.8 | 11 | † |

* The properties given here relate to platinum to which 0.5% of another noble metal has been added to give slightly greater hardness This grade is invariably used for electrical contacts

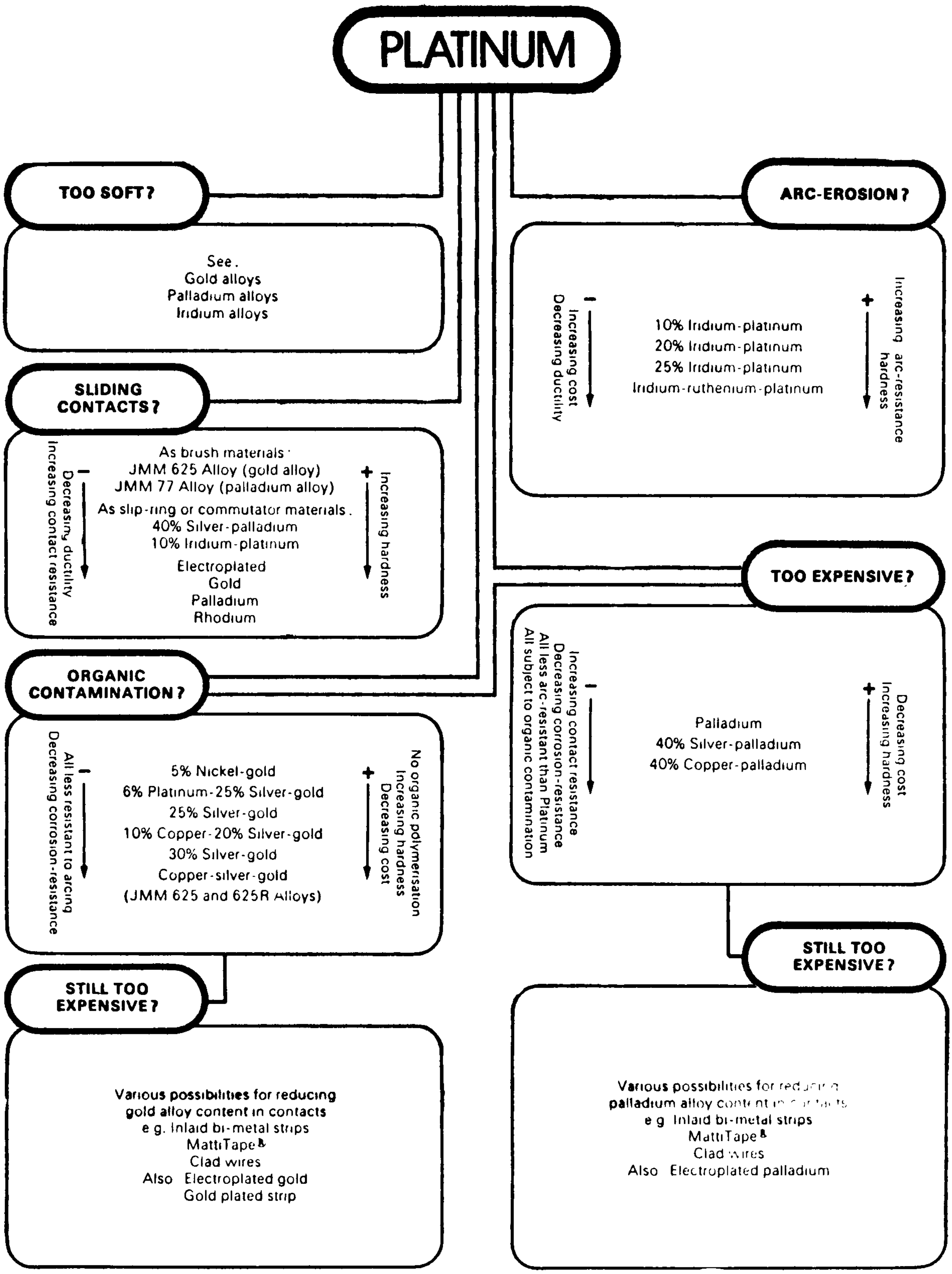
** These figures apply to electrodeposited forms of the metals

*** Can also be supplied hard 200-240 HV or 250 HV minimum

† Where thermal conductivity figures are not available, an approximate value can be obtained from the electrical conductivity figures, which vary in direct proportion

†† Figures for solution treated material hardness can be increased to 300-370 HV minimum by age hardening (see data sheet 1300 512)

# Light duty contacts



**PLATINUM**

**TOO SOFT?**

See.
Gold alloys
Palladium alloys
Iridium alloys

**SLIDING CONTACTS?**

As brush materials:
JMM 625 Alloy (gold alloy)
JMM 77 Alloy (palladium alloy)
As slip-ring or commutator materials.
40% Silver-palladium
10% Iridium-platinum
Electroplated
Gold
Palladium
Rhodium

− Increasing contact resistance
Decreasing ductility

\+ Increasing hardness

**ORGANIC CONTAMINATION?**

5% Nickel-gold
6% Platinum-25% Silver-gold
25% Silver-gold
10% Copper-20% Silver-gold
30% Silver-gold
Copper-silver-gold
(JMM 625 and 625R Alloys)

− Decreasing corrosion-resistance
All less resistant to arcing

\+ No organic polymerisation
Increasing hardness
Decreasing cost

**STILL TOO EXPENSIVE?**

Various possibilities for reducing
gold alloy content in contacts
e g. Inlaid bi-metal strips
MattiTape®
Clad wires
Also Electroplated gold
Gold plated strip

**ARC-EROSION?**

10% Iridium-platinum
20% Iridium-platinum
25% Iridium-platinum
Iridium-ruthenium-platinum

− Decreasing ductility
Increasing cost

\+ Increasing arc-resistance
hardness

**TOO EXPENSIVE?**

Palladium
40% Silver-palladium
40% Copper-palladium

− All subject to organic contamination
All less arc-resistant than Platinum
Decreasing corrosion-resistance
Increasing contact resistance

\+ Decreasing cost
Increasing hardness

**STILL TOO EXPENSIVE?**

Various possibilities for reducing
palladium alloy content in contacts
e g Inlaid bi-metal strips
MattiTape®
Clad wires
Also Electroplated palladium

# Typical properties of medium duty contact materials

**SILVER-BASED MATERIALS**

| MATERIAL | | Specific Gravity | Hardness (Annealed), HV | Melting Point (Solidus), °C | Specific Resistance, μΩ cm | Electrical Conductivity, %IACS | Thermal Conductivity, Approximate W/mK |
|---|---|---|---|---|---|---|---|
| **SILVER** | Fine Silver | 10.5 | 26<br>80–110** | 962 | 1.6 | 106 | 420 |
| | JMM 1715 Alloy† | 10.4 | 145 | 962 | 2.8 | 60 | 275 |
| | 3% copper-silver (Hardsilver) | 10.4 | 40 | 778 | 1.7 | 95 | 390 |
| | 7½% copper-silver (Standard silver) | 10.3 | 56 | 778 | 1.9 | 90 | 350 |
| | 10% copper-silver | 10.3 | 62 | 778 | 2.0 | 86 | 345 |
| | 20% copper-silver | 10.2 | 85 | 778 | 2.1 | 82 | 335 |
| | 50% copper-silver | 9.7 | 95 | 778 | 2.1 | 82 | 315 |
| | 10% gold-silver | 11.0 | 29 | 965 | 3.6 | 48 | 230 |
| | 5% palladium-silver | 10.5 | 33 | 965 | 3.8 | 45 | 220 |
| | 10% palladium-silver | 10.6 | 40 | 1000 | 5.8 | 30 | 145 |
| | 20% palladium-silver | 10.7 | 55 | 1070 | 10.1 | 17 | 90 |
| | 30% palladium-silver | 10.8 | 67 | 1170 | 16.0 | 11 | 50 |
| **CADMIUM OXIDE-SILVER** | Matthey D54 | 9.8 | 50 | – | 2.1 | 82 | 370 |
| | Matthey D55 | 9.6 | 55 | – | 2.3 | 72 | 350 |
| | Matthey D54X | 10.0 | 58 | – | 2.1 | 82 | 370 |
| | Matthey D55X | 9.8 | 60 | – | 2.3 | 75 | 355 |
| **NICKEL-SILVER** | Matthey D510 | 10.3 | 40 | – | 2.0 | 87 | 365 |
| | Matthey D520 | 10.1 | 48 | – | 2.1 | 82 | †† |
| | Matthey D56 | 9.9 | 68 | – | 2.4 | 72 | 310 |
| **GRAPHITE-SILVER** | Matthey D58–2% | 9.7 | 40 | – | 2.0 | 86 | 375 |
| | Matthey D58–1% | 9.9 | 40 | – | 1.8 | 96 | †† |

* For electrical contacts Fine Silver has a purity of 99.9% minimum.

** These figures apply to the electrodeposited form

† Oxidation hardened

†† Where thermal conductivity figures are not available, an approximate value can be obtained from the electrical conductivity figures, which vary in direct proportion.

# Medium duty contacts

## FINE SILVER

### SLIDING CONTACTS?

−
Increasing contact resistance
Decreasing ductility

As brush materials:
1% Graphite-silver
(Matthey D58-1%)
2% Graphite-silver
(Matthey D58-2%)
5% Graphite-silver
(Matthey D58-5%)

As slip-ring
or commutator materials:
Electroplated silver
Also: See Copper-silvers
See Palladium-silvers

\+
Increasing lubrication
Increasing weld-resistance

### WELDING?

−
Increasing contact resistance
Decreasing ductility
Decreasing conductivity

10% Cadmium oxide-silver
(Matthey D54 and D54X)
15% Cadmium oxide-silver
(Matthey D55 and D55X)

Also: See Palladium-silvers
See Graphite-silvers

\+
Increasing: weld-resistance
arc-resistance
hardness

### HIGH CONTACT RESISTANCE? (TARNISHING)

−
Increasing cost
Decreasing conductivity

5% Palladium-silver
10% Palladium-silver
20% Palladium-silver
30% Palladium-silver

Also: 10% Gold-silver

\+
Increasing: tarnish-resistance
hardness
weld-resistance

### ARC-EROSION?

−
Decreasing conductivity
Decreasing ductility
Increasing tarnish
Increasing contact resistance

10% Nickel-silver
(Matthey D510)
20% Nickel-silver
(Matthey D520)
30% Nickel-silver
(Matthey D56)

Also: See Palladium-silvers
See Copper-silvers

\+
Increasing arc-resistance
Increasing hardness

### TOO SOFT?

−
Increasing tarnish
Increasing contact resistance

3% Copper-silver (Hardsilver)
7½% Copper-silver (Standard Silver)
10% Copper-silver
20% Copper-silver
50% Copper-silver

Also: Electroplated silver
Nickel-magnesium-silver (JMM 1715 Alloy)
See Palladium-silvers
See Silver-cadmium oxides
See Nickel-silvers

\+
Increasing hardness
Increasing arc-resistance
Decreasing cost

### TOO EXPENSIVE?

Various possibilities for reducing
silver content in contacts
e.g. Optecon® silver-faced copper rivets
Silver-on-steel button contacts
Welded contact assemblies
Pressmattic® contact strips
Inlaid and onlaid bi-metal strips
Silver-faced MattiTape®

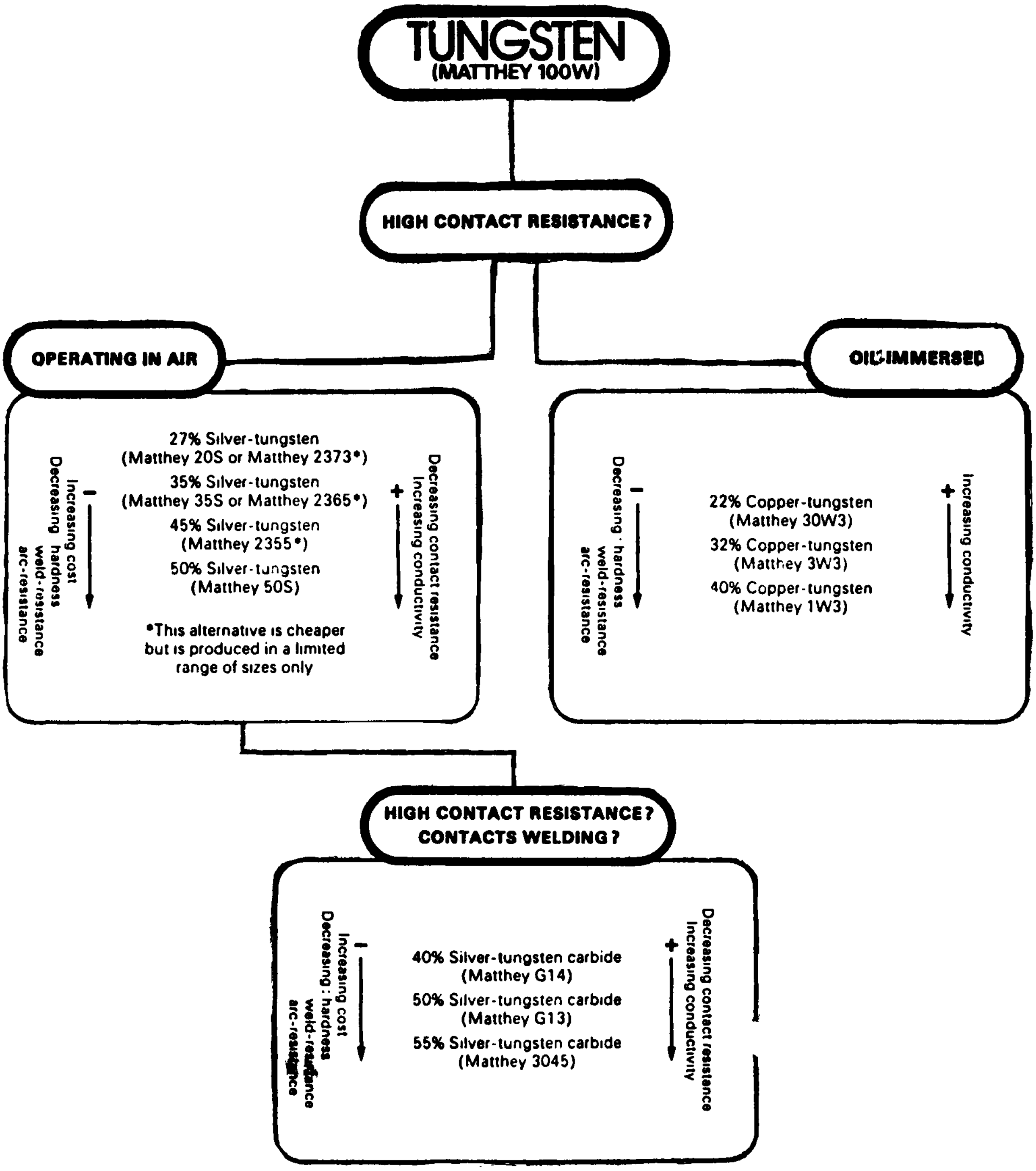
Also: See Copper-silvers

# Typical properties of heavy duty sintered contact materials

**TUNGSTEN-BASED MATERIALS**

| MATERIAL | | Specific Gravity | Hardness (Annealed), HV | Melting Point (Solidus), °C | Specific Resistance, μΩ cm | Electrical Conductivity, %IACS | Thermal Conductivity, Approximate W/mK |
|---|---|---|---|---|---|---|---|
| **TUNGSTEN** | Matthey 100W | 19.3 | 290 | 3387 | 5.5 | 31 | 145 |
| **SILVER-TUNGSTEN** | Matthey 20S | 15.6 | 220 | – | 4.0 | 43 | 220 |
| | Matthey 35S | 14.8 | 140 | – | 3.3 | 52 | 235 |
| | Matthey 50S | 13.6 | 115 | – | 2.8 | 61 | 275 |
| | Matthey 2373 | 14.9 | 180 | – | 3.8 | 45 | 225 |
| | Matthey 2365 | 14.6 | 135 | – | 3.4 | 50 | 230 |
| | Matthey 2355 | 13.8 | 125 | – | 2.8 | 60 | 274 |
| **SILVER-TUNGSTEN CARBIDE** | Matthey G14 | 13.2 | 200 | – | 4.8 | 36 | 160 |
| | Matthey G13 | 12.5 | 110 | – | 3.0 | 57 | 265 |
| | Matthey 3045 | 12.2 | 95 | – | 2.7 | 62 | 275 |
| **COPPER-TUNGSTEN** | Matthey 30W3 | 15.2 | 240 | – | 6.1 | 28 | 140 |
| | Matthey 3W3 | 13.6 | 160 | – | 5.3 | 33 | 150 |
| | Matthey 1W3 | 12.8 | 140 | – | 4.6 | 41 | 210 |

# Heavy duty sintered contacts



**OPERATING IN AIR**

27% Silver-tungsten
(Matthey 20S or Matthey 2373*)

35% Silver-tungsten
(Matthey 35S or Matthey 2365*)

45% Silver-tungsten
(Matthey 2355*)

50% Silver-tungsten
(Matthey 50S)

*This alternative is cheaper but is produced in a limited range of sizes only

**OIL-IMMERSED**

22% Copper-tungsten
(Matthey 30W3)

32% Copper-tungsten
(Matthey 3W3)

40% Copper-tungsten
(Matthey 1W3)

**HIGH CONTACT RESISTANCE? CONTACTS WELDING?**

40% Silver-tungsten carbide
(Matthey G14)

50% Silver-tungsten carbide
(Matthey G13)

55% Silver-tungsten carbide
(Matthey 3045)

## LME - Ring-Dealer Members

1. Amalgamated Metal Trading Ltd.
2. Ametalco Trading Ltd.
3. Anglo Chemical Metals Ltd.
4. Associated Lead Manufacturers Ltd.
5. Henry Bath & Son Ltd.
6. Billiton Enthoven Metals Ltd.
7. Boustead Davis (Metal Brokers) Ltd.
8. Brandeis, Goldschmidt & Co. Ltd.
9. Cerro Metals (UK) Ltd.
10. Cominco (UK) Ltd.
11. The Commercial Metal Co. Ltd.
12. Continental Ore Europe Ltd.
13. Entores (Metal Brokers) Ltd.
14. Gerald Metals Ltd.
15. Gill & Duffers Ltd.
16. Intsel Ltd.
17. Leopold Lazarus Ltd.
18. Lonconex Ltd.
19. Maclaine, Watson & Co. Ltd.
20. Metallgesellschaft Ltd.
21. Metdist Ltd.
22. Philipp & Lion

Appendix 5
(continued)

23. J.H. Rayner (Mincing Lane) Ltd.
24. Sharps, Pixley Ltd.
25. Sogemin Metals Ltd.
26. Tennant Trading Metals Ltd.
27. H.P. Thompson & Sons Ltd.
28. Triland Metals Ltd.
29. Wilson Smithett & Cope Ltd.
30. Rudolf Wolff & Co. Ltd.

# LIST OF APPENDICES

1. Ag recovery methods applied to photography scrap materials.
2. Imports of unwrought silver and silver alloys by country of origin in France, West Germany, Italy, the Netherlands , the United Kingdom.
3. Raw silver imports and exports within the EEC countries in 1977.
4. Typical properties of contact materials.
5. LME - Ring-Dealer Members.

# LIST OF TABLES AND SOURCES

1.1.a. Ag reserves and resources by countries.
- US Geological Survey.

1.1.b. Main primary silver producers in Canada.
- Companies' Annual reports, SGM copper, zinc and lead mines data bases.

1.1.c. Main primary silver producers in the USA.
- Companies' Annual reports, SGM copper, zinc and lead mines data bases.

1.1.d. Main primary silver refineries in the USA.
- Companies' Annnual reports, SGM copper data base.

1.1.e. Primary silver production in the EEC.
- Companies' Annual reports, Dossier on lead and zinc and Dossier on copper prepared for the Commission of the European Communities DG XII (April and June 1979).

1.1.f. 1985 Primary silver production - mt Ag.
- Estimated figures.

1.2.a. Sales of Indian silver.
- Handy & Harman Annual Reviews and press informations.

1.2.b. Silver imports from India in the EEC countries - mt Ag - 1974-1978.
- Import-Export national statistics (items 71 05 010 to 71 05 030).

1.2.c. World industrial silver scrap supply - mt Ag - 1970-1978.
- Handy & Harman Annual Reviews.

1.2.d. World silver supply from demonetized coins - mt Ag - 1970-1978.
- Handy & Harman Annual Reviews.

1.2.e. 1978 Silver stocks - mt Ag.
- Handy & Harman Annual Reviews.

1.3.a. EEC silver industry.
- Companies' Annual reports, Non-Ferrous Metals Works of the World (Metal Bulletin 1974), press and "calls" informations.

1.3.b. EEC imports of unwrought silver in 1977 - mt Ag
- Import national statistics (items 71 05 010 to 71 05 030).

2.1.a. 1978 Silver consumption in the photography industry - mt Ag

- Handy & Harman Annual Reviews for the USA.
- Sumitomo's publication on non-ferrous metals, aluminium, precious metals in Japan, April 1979 for Japan.
- Calls informations and Handy & Harman's figures for the EEC countries.

2.1.b. Sensitive surfaces production in the EEC by type of application.

2.2.a. 1978 Consumption of silver by the elec-electronic industry - mt Ag.

- Same sources as in 2.1.a.

2.2.b. Battery producers in the EEC.

2.3.a. 1978 Silver consumption in brazing alloys - mt Ag.

- Same sources as in 2.1.a.

2.4.a. 1978 Silver consumption in jewelry and silverware - mt Ag

- Same sources as in 2.1.a.

2.5.a. 1978 Silver consumption in "other uses" - mt Ag.

- Same sources as in 2.1.a.

2.6.a. Silver consumption for coinage - mt Ag, 1970-1978.

- Handy & Harman Annual Reviews.

2.8.a. 1978 Silver consumption in EEC countries - mt Ag.

- Estimations and Handy & Harman Annual Reviews for French, German, Italian and British total industrial silver consumption figures.

2.8.b. The 1985 outlook for silver consumption in the EEC - mt Ag.

- Estimations.

2.8.c. 1985 Expected Ag consumption by the EEC industry.

- Estimations.

5.1.a. 1978 Silver consumption in EEC countries.

- Same sources as in 2.8.a.

5.1.b. The 1985 outlook for silver consumption in the EEC - mt Ag.

- Estimations.

5.3.a. Industrial silver consumption in the EEC countries by 1985-1990.

- Estimations.

## LIST OF GRAPHS

# CONTACTS

## Photography industry

| | |
|---|---|
| - Agfa-Gevaert N.V.<br>Mortsel (Antwerp) - Belgium. | SGM |
| - Kodak Pathé,<br>Paris - France. | BIPE |
| - Syndicat des Surfaces Sensibles,<br>Paris, France. | BIPE |
| - Ilford,<br>Brentwood, Essex - United Kingdom. | BIPE |

## Electrical and electronic industry

| | |
|---|---|
| - Laboratoire Central des Industries<br>Electriques et Electroniques,<br>Paris - France. | BIPE |
| - Centre National des Etudes Télécommunication,<br>Lannion, France. | BIPE |
| - Jean Renard,<br>Dôle, France. | BIPE |
| - Merlin Gérin,<br>Grenoble, France. | BIPE |
| - Sfernice,<br>Nice, France. | BIPE |
| - Télémécanique Electrique,<br>Nanterre, France. | BIPE |
| - Secmé,<br>Bagnolet, France. | BIPE |
| - SOGEA,<br>Romainville, France. | BIPE |
| - Mec-Betras,<br>Lentate s/Seresa, Italy. | BIPE |
| - Crouzet SpA,<br>Milan, Italy. | BIPE |
| - Siemens Elettra,<br>Milan, Italy. | BIPE |

| | |
|---|---|
| - Electrical Research Association,<br>Leatherhead, Surrey, United Kingdom. | BIPE |
| - Berec Micro Batteries,<br>Banbury-Oxon, United Kingdom. | BIPE |

## Brazing alloys and soldering

| | |
|---|---|
| - Institut de la Soudure,<br>Paris, France. | BIPE |
| - Centre Scientifique et Technique du Bâtiment,<br>Paris, France. | BIPE |
| - Union des Chambres Syndicales de Couverture-Plomberie,<br>Paris, France | BIPE |
| - Chambre Syndicale des Fabricants de Brasure,<br>Paris, France. | BIPE |
| - Building Research Establishment,<br>Garston, Watford, United Kingdom. | BIPE |

## Coinage

| | |
|---|---|
| - Monnaie Royale de Belgique,<br>Brussels, Belgium. | SGM |
| - Administration des Monnaies et Médailles,<br>Paris, France. | BIPE |

## Silver metallurgical producers, refiners, fabricators

| | |
|---|---|
| - Metallurgie Hoboken-Overpelt,<br>Hoboken, Belgium. | SGM |
| - Etma,<br>Wilsele (**Malines**), Belgium | SGM |
| - Comptoir Lyon Alemand Louyot,<br>Paris, France. | BIPE |
| - Degussa,<br>Frankfort, West Germany. | SGM |
| - Metalli Preziosi,<br>Paderno Dugnano, Italy. | BIPE |
| - Mario Villa,<br>Milan, Italy. | BIPE |

| | |
|---|---|
| - Chimi Foto Ornano,<br>Milan, Italy | BIPE |
| - Engelhard Industries,<br>Sutton, Surrey, United Kingdom. | BIPE |
| - Johnson Matthey Metals,<br>London, United Kingdom. | BIPE |
| - Johnson Matthey Chemicals,<br>Royston, United Kingdom. | BIPE |
| - NRC National Refining Corporation,<br>Gallatin, Tennessee, USA. | SGM |
| - J. Aron & Company,<br>New York, USA. | SGM |

Miscellaneous

| | |
|---|---|
| - Fédération des Industries de<br>Métaux Non Ferreux,<br>Brussels, Belgium. | SGM |
| - Peri-MP,<br>St.Germain-en-Laye, France. | BIPE |

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COMMISSION OF THE EUROPEAN COMMUNITIES
(Directorate General XII - Research, Science and Education)

# CHROMIUM SUBSTITUTION STUDY

A report

by

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November 1979

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Under the supervision of: L Whalley

Approved by: D V Jackson

Period covered by report: March - November 1979

Illustration reference numbers:
Fig. 1 L-11402-MR (from IGS)
Fig. 2 L-11403-MR (from IGS)
Fig. 3 L-11404-MR (from IGS)
Fig. 4 from IGS
Fig. 5 from IGS
Fig. 6 L-11363-MR
Fig. 7 L-11405-MR
Fig. 8 L-11367-MR (from reference 1)
Fig. 9 L-11365-MR
Fig. 10 L-11366-MR

# CONTENTS

# CREST CHROMIUM SUBSTITUTION STUDY:

## FINAL REPORT

L. Whalley, G.O. Lloyd (NPL), C. Neary (IGS)

## SUMMARY

This report reviews the use of chromium and chromium-bearing materials in their metallurgical, refractory, and chemical applications. Sources of chromium supplies to the Community and end-use consumption patterns are discussed and an attempt is made to define the most critical applications. Proposals are made for a Community R and D programme to promote conservation of chromium by the development of acceptable substitute materials.

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This report was originally submitted as report CR 1724(MR) from the Warren Spring Laboratory.

## 1. INTRODUCTION

Chromium and chromium-bearing materials are vitally important commodities to industry in the EEC. Although reserves of chromite are very plentiful in comparison with most other metal ores, they are concentrated in only a few countries. Two countries, South Africa and Rhodesia, possess well over 90% of the world's reserves, and only two other countries possess a proportion of 1% or more. The Community is therefore vulnerable to interruptions in supply as a result of possible future economic or political pressures. The purpose of this study is to investigate whether or not a Community R and D programme might be capable of developing alternative materials for important end-uses of chromium. In order to do this, the available data on sources, consumption and end-use patterns are presented and interpreted in the early chapters of the report. Known substitute materials are identified and the economic and technical impact of substitution is discussed. As far as possible, on the basis of available information, critical end-uses are defined, and R and D proposals are aimed at developing new substitute materials for critical applications. At the request of the co-pilots some attention is also paid to the conservation of chromium by recycling or development of new processes for existing applications, although these topics are not strictly materials subtitution.

In this study the United Kingdom has acted as pilot country with Warren Spring Laboratory (WSL) as project leaders assisted by the National Physical Laboratory (NPL) and the Institute of Geological Sciences (IGS). The co-pilots were Italy, represented by Fiat Engineering and Holland, represented by TNO. The authors are also grateful to other national delegations to the CREST Substitution Working Group for their assistance in providing information.

The Italian report is included here as Appendix A. On behalf of The Netherlands TNO have produced two reports on aspects of chromium plating technology. These have been submitted independently, but an extract is included here as Appendix B.

## 2. SUPPLIES OF CHROMIUM TO THE COMMUNITY

### 2.1 Sources of Chromite

#### 2.1.1 World Production

Chromite is the only commercial source of chromium. Commercial extraction of chromite first took place in the late 18th century and by 1936 world annual production exceeded 1 million tonnes. In the late 1970's world production is rapidly approaching 10 million tonnes (Fig. 1, Table 1). Between 1950 and 1976 production of chromite increased by an annual average of 3.9%*.

During the last twenty five years the distribution of production has become progressively less diversified. Until the early 1960's there were at least five countries each producing between 10 and 20% of the world's supply (Table 2). Since 1966 South Africa and USSR have each produced over 20% of the world's annual production with the nearest rivals all producing less than 10%, and most of them (Turkey, Rhodesia, Philippines) continuously declining in importance. Only Albania shows a steady increase in output (Fig. 2). Especially noticeable is the absence of production in North America and Western Europe (Fig. 3), both areas of high consumption.

Chromite for refractory and chemical use is generally shipped directly to the consuming industry so that countries of origin indicated for this material are countries where it is mined. Where chromite is used for metallurgical purposes, however, it passes through an intermediate stage in the form of the alloy ferrochromium. The country which is a producer and exporter of ferrochromium for example, may well have

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(*Best fit logarithmic curve, correlation coefficient 0.95; source Mineral Statistics and Economics Unit MSEU at IGS.)

TABLE 1. - World Chromite Production (million tonnes)

| Year | Production | Year | Production | Year | Production | Year | Production |
|---|---|---|---|---|---|---|---|
| 1910 | | 1930 | 0.559 | 1950 | 2.34 | 1970 | 6.11 |
| 11 | | 31 | 0.314 | 51 | 2.79 | 71 | 6.36 |
| 12 | | 32 | 0.299 | 52 | 3.35 | 72 | 6.27 |
| 13 | 0.118 | 33 | 0.409 | 53 | 3.60 | 73 | 6.79 |
| 14 | 0.132 | 34 | 0.629 | 54 | 3.38 | 74 | 7.57 |
| 15 | 0.170 | 35 | 0.792 | 55 | 3.64 | 75 | 8.28 |
| 16 | 0.266 | 36 | 1.06 | 56 | 4.11 | 76 | 8.55 |
| 17 | 0.249 | 37 | 1.25 | 57 | 4.57 | 77 | 9.46 |
| 18 | 0.274 | 38 | 1.13 | 58 | 3.72 | | |
| 19 | 0.091 | 39 | 1.18 | 59 | 3.99 | | |
| 1920 | 0.081 | 1940 | 1.37 | 1960 | 4.40 | | |
| 21 | 0.135 | 41 | 1.65 | 61 | 4.22 | | |
| 22 | 0.145 | 42 | 1.99 | 62 | 4.31 | | |
| 23 | 0.203 | 43 | 1.75 | 63 | 4.05 | | |
| 24 | 0.281 | 44 | 1.46 | 64 | 4.24 | | |
| 25 | 0.315 | 45 | 1.14 | 65 | 4.90 | | |
| 26 | 0.366 | 46 | 1.17 | 66 | 4.83 | | |
| 27 | 0.406 | 47 | 1.62 | 67 | 4.66 | | |
| 28 | 0.447 | 48 | 1.97 | 68 | 5.38 | | |
| 29 | 0.599 | 49 | 2.16 | 69 | 5.36 | | |

| | | |
|---|---|---|
| Source: | 1913-1949 | The Mineral Industry of the British Empire and Foreign Countries |
| | 1950-1969 | Statistical Summary of the Mineral Industry |
| | 1970-1974 | World Mineral Statistics |
| | 1974-1977 | MSEU |

imported chromite for the purpose. The sources of intermediates may themselves be dependent on exporters of chromite, a factor which must be remembered when sources of chromium are being considered.

### 2.1.2 World Reserves and Resources of Chromite

Estimated world chromite reserves are given in Table 4. The imbalance in the geographical distribution of reserves is clearly even greater than that of production. Two countries, South Africa and Rhodesia, possess well over 90% of the world's reserves. The USSR with 2% and Finland with 1% are the only other countries with a proportion of 1% or more.

Several countries contain significant resources (e.g. Greenland, USA) although at present these are not exploited for technical and economic reasons.

It is essential to bear in mind that figures quoted for reserves and resources are dynamic in nature. In the case of reserves, they are the sum of individual mines' operating reserves, and as such are constantly being extended as far as possible in advance of mining in order to ensure the continued life of those mines. Resources (which includes reserves) comprise all deposits from which economic extraction of minerals is currently or potentially feasible; since this definition includes undiscovered resources, only thought to exist, the figures must be viewed with caution.

From the above caveat it follows that simple comparisons of reserves (or resources) with current annual production made in order to arrive at a figure for the theoretical life of the reserves have relatively limited value. For any single mine such a figure is usually between 5 and 25 years, although for national totals this may be augmented by reserves in undeveloped deposits. Nevertheless, Table 5 shows such a calculation for chromite reserves and resources. It is worth noting the dramatic decrease in the theoretical life of reserves and resources at modest production growth rates (the 'dynamic' columns), compared with that for the 'static' ('zero growth')

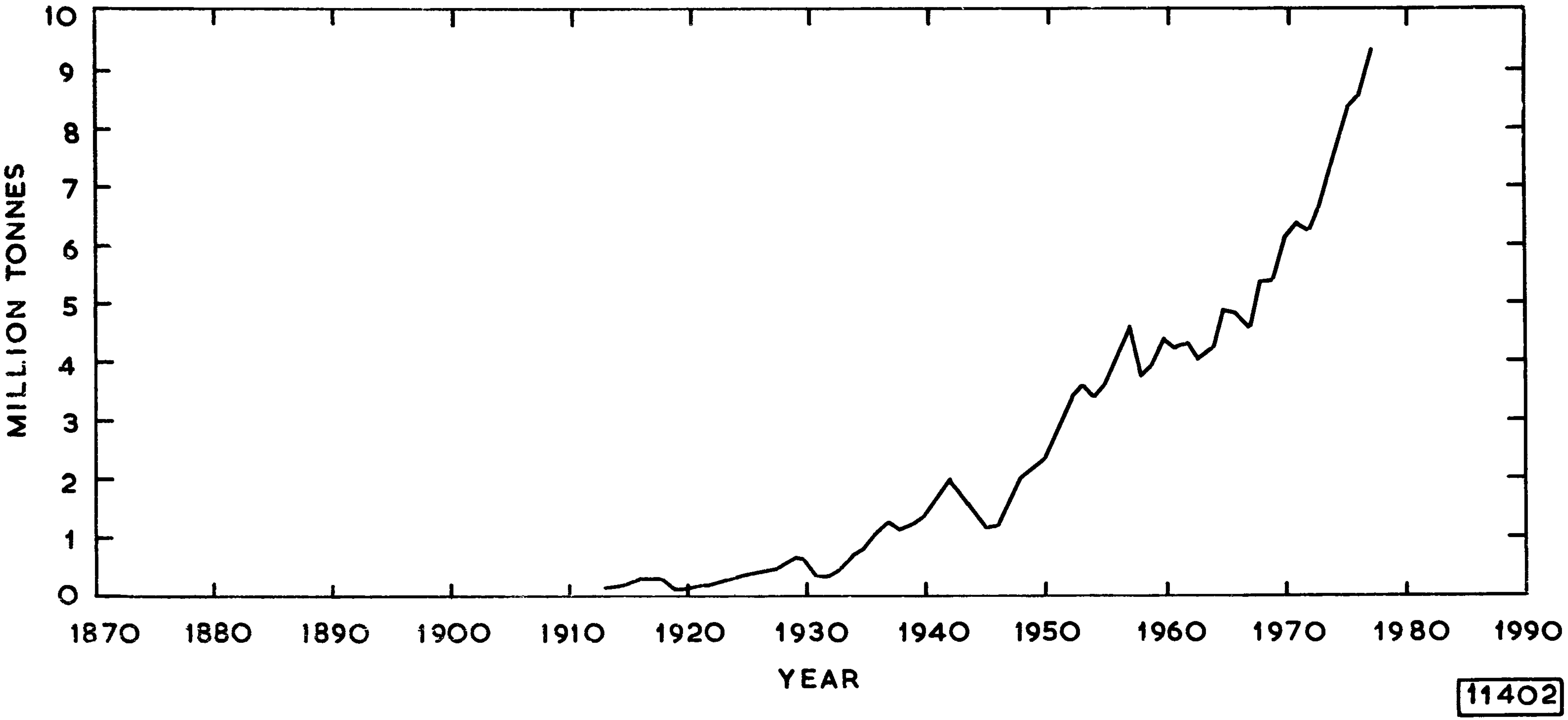

FIG. 1 WORLD CHROMITE PRODUCTION 1913 – 1977

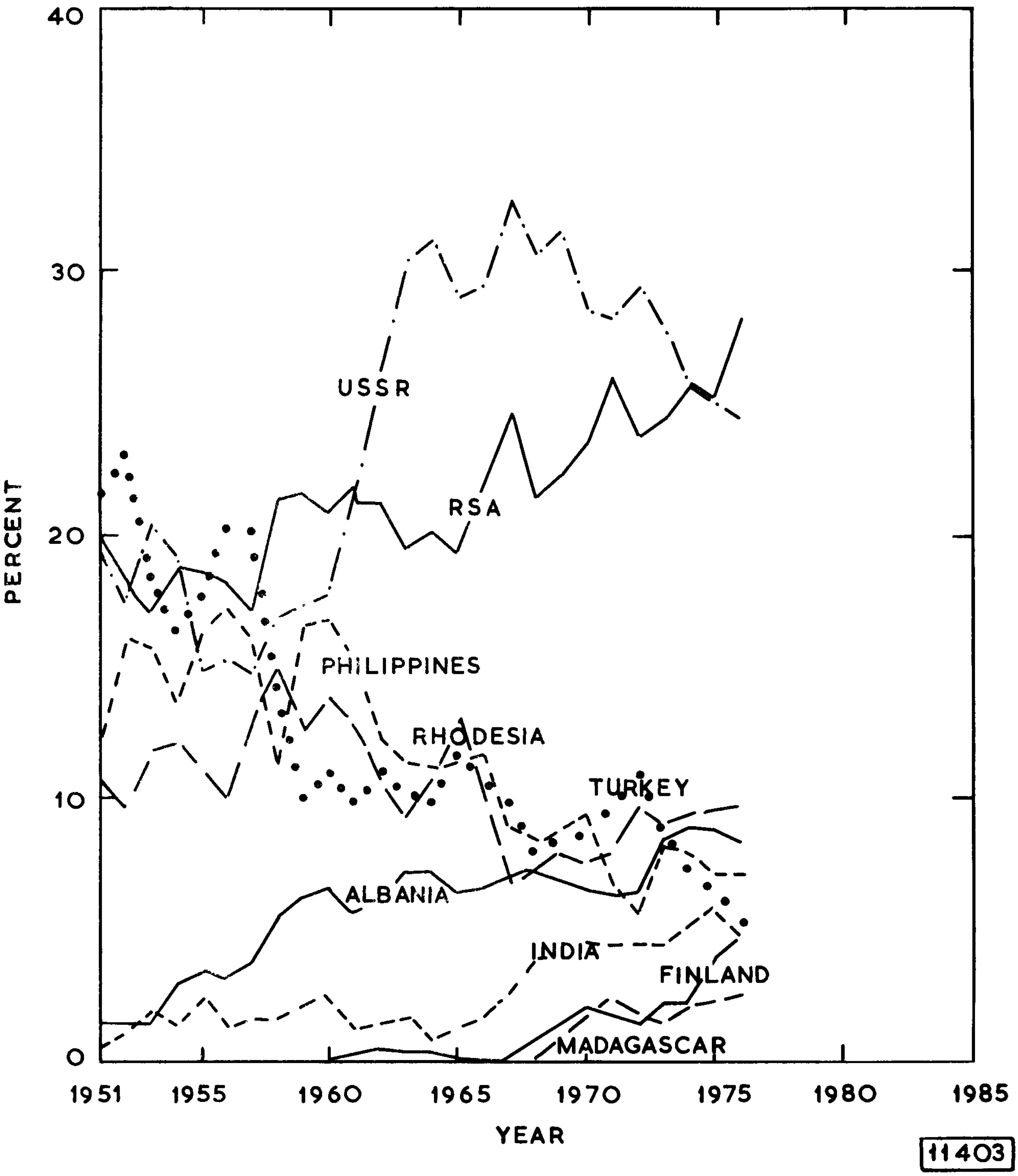

FIG. 2 WORLD CHROMITE PRODUCTION PERCENTAGE SHARE: MAJOR PRODUCERS 1951 - 76

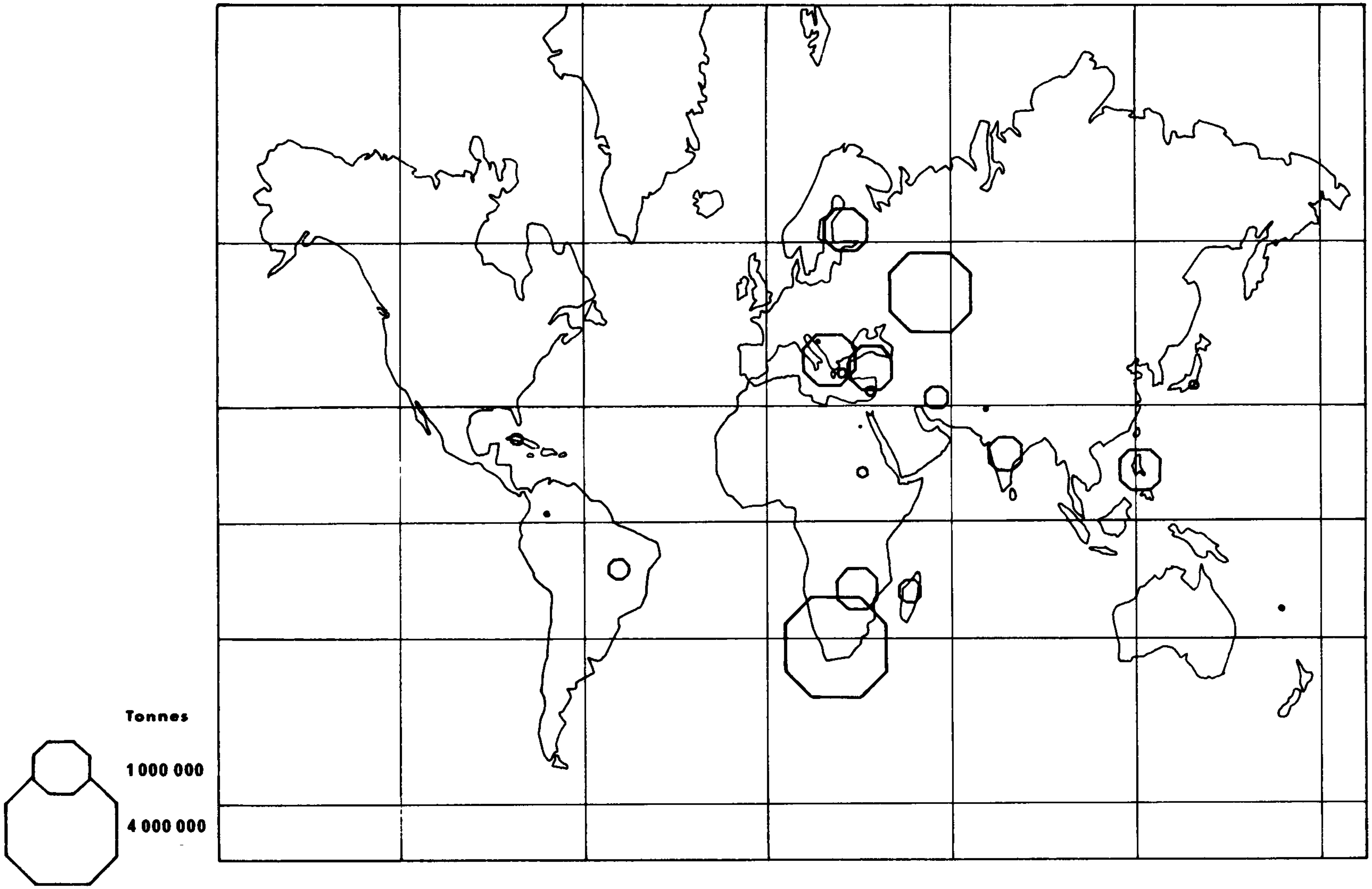

FIG. 3 WORLD PRODUCTION OF CHROMITE 1977

TABLE 2. - Chromite Production (% of World Production)

| Country | 1951 | 1952 | 1953 | 1954 | 1955 | 1956 | 1957 | 1958 | 1959 | 1960 | 1961 | 1962 | 1963 | 1964 | 1965 | 1966 | 1967 | 1968 | 1969 | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S.Africa | 19.5 | 17.3 | 20.4 | 19.1 | 14.8 | 15.2 | 14.6 | 16.8 | 17.2 | 17.5 | 21.3 | 21.2 | 19.5 | 20.1 | 19.2 | 21.9 | 24.7 | 21.4 | 22.2 | 23.4 | 25.9 | 23.7 | 24.3 | 25.8 | 25.1 | 28.2 |
| USSR | 20.0 | 18.2 | 16.9 | 18.8 | 18.6 | 18.0 | 16.9 | 21.4 | 21.5 | 20.8 | 21.8 | 26.7 | 30.3 | 31.2 | 29.0 | 29.4 | 32.6 | 30.6 | 31.6 | 28.6 | 28.3 | 29.5 | 28.0 | 25.7 | 25.1 | 24.6 |
| Albania | 1.6 | 1.5 | 1.5 | 3.0 | 3.4 | 3.2 | 3.7 | 5.4 | 6.2 | 6.5 | 5.5 | 5.9 | 7.2 | 7.2 | 6.3 | 6.5 | 7.0 | 7.2 | 8.0 | 7.6 | 7.9 | 9.7 | 9.0 | 9.4 | 9.4 | 9.7 |
| Turkey | 21.4 | 23.1 | 18.2 | 16.1 | 17.6 | 20.2 | 20.0 | 13.9 | 9.8 | 10.9 | 9.6 | 10.9 | 10.0 | 9.7 | 11.6 | 10.6 | 9.6 | 7.8 | 8.4 | 8.5 | 9.5 | 10.8 | 8.4 | 8.8 | 8.7 | 8.3 |
| Rhodesia | 10.7 | 9.6 | 11.8 | 12.0 | 11.1 | 9.9 | 13.0 | 14.9 | 12.4 | 13.8 | 12.7 | 10.7 | 9.2 | 10.6 | 12.9 | 10.5 | 6.8 | 7.1 | 6.8 | 6.5 | 6.3 | 6.4 | 8.1 | 7.8 | 7.1 | 7.1 |
| Philippines | 12.0 | 16.2 | 15.7 | 13.5 | 16.3 | 17.2 | 15.9 | 11.1 | 16.5 | 16.7 | 15.2 | 12.3 | 11.3 | 11.1 | 11.3 | 11.6 | 9.0 | 8.2 | 8.7 | 9.3 | 6.8 | 5.6 | 8.5 | 7.0 | 6.3 | 5.0 |
| India | 0.6 | 1.1 | 1.9 | 1.4 | 2.5 | 1.3 | 1.7 | 1.7 | 2.2 | 2.4 | 1.2 | 1.5 | 1.6 | 0.8 | 1.2 | 1.6 | 2.4 | 3.8 | 4.2 | 4.5 | 4.3 | 4.5 | 4.3 | 5.2 | 6.0 | 4.7 |
| Madagascar | - | - | - | - | - | - | - | - | - | - | 0.2 | 0.4 | 0.3 | 0.3 | 0.05 | - | - | - | 0.8 | 1.7 | 2.4 | 1.8 | 1.5 | 2.1 | 2.3 | 2.5 |
| Finland | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.1 | 0.7 | 1.3 | 2.0 | 1.8 | 1.5 | 2.2 | 2.2 | 4.0 | 4.8 |
| Iran | 0.3 | 0.6 | 0.5 | 0.4 | 0.3 | 0.6 | 0.8 | 1.3 | 1.7 | 1.5 | 1.7 | 2.5 | 2.4 | 2.9 | 0.3 | 2.9 | 3.2 | 3.0 | 3.4 | 3.6 | 3.1 | 2.2 | 2.1 | 2.3 | 1.9 | 1.9 |
| Brazil | 0.1 | 0.1 | 0.1 | 0.06 | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.4 | 0.6 | 1.1 | 0.6 | 0.7 | 0.5 | 0.3 | 0.3 | 0.3 | 0.6 | 0.9 | 1.1 | 1.1 | 1.2 | 1.9 | 1.5 |
| Cuba | 2.8 | 1.8 | 2.1 | 2.2 | 2.7 | 1.2 | 3.3 | 2.0 | 1.0 | 6.8 | 0.6 | 0.8 | 1.4 | 0.8 | 0.6 | 0.6 | 0.6 | 0.9 | 0.9 | 0.4 | 0.2 | 0.6 | 0.5 | 0.5 | 0.5 | 0.4 |
| Sudan | - | - | - | - | - | - | - | - | - | - | - | 0.2 | 0.4 | 0.4 | 0.6 | 0.4 | 0.4 | 0.4 | 0.5 | 0.8 | 0.3 | 0.4 | 0.5 | 0.3 | 0.4 | 0.3 |
| Japan | 1.5 | 1.4 | 1.1 | 1.0 | 0.7 | 1.0 | 1.0 | 1.1 | 1.5 | 1.5 | 1.7 | 1.3 | 1.1 | 1.0 | 0.9 | 0.7 | 1.0 | 0.5 | 0.6 | 0.5 | 0.5 | 0.4 | 0.3 | 0.4 | 0.3 | 0.3 |
| Cyprus | 0.4 | 0.4 | 0.2 | 0.3 | 0.2 | 0.2 | 0.1 | 0.3 | 0.3 | 0.5 | 0.4 | 0.2 | 0.1 | - | 0.1 | 0.2 | 0.5 | 0.5 | 0.4 | 0.5 | 0.6 | 0.5 | 0.4 | 0.4 | 0.3 | 0.1 |
| Pakistan | 0.6 | 0.5 | 0.7 | 0.7 | 0.8 | 0.6 | 0.4 | 0.6 | 0.4 | 0.4 | 0.6 | 0.5 | 0.4 | 0.3 | 0.3 | 0.6 | 0.6 | 0.5 | 0.5 | 0.4 | 0.5 | 0.5 | 0.3 | 0.1 | 0.1 | 0.1 |
| Greece | 0.9 | 1.0 | 1.0 | 0.8 | 0.7 | 1.9 | 1.6 | 1.7 | 1.6 | 1.0 | 1.8 | 1.3 | 1.3 | 0.9 | 1.0 | 1.0 | 0.2 | 0.2 | 0.5 | 0.4 | 0.2 | 0.4 | 0.3 | 0.1 | 0.3 | 0.3 |
| Yugoslavia | 3.6 | 3.2 | 3.6 | 3.7 | 3.5 | 2.9 | 2.6 | 3.0 | 2.7 | 2.3 | 2.6 | 2.3 | 2.3 | 2.1 | 1.6 | 1.1 | 1.0 | 0.8 | 0.7 | 0.7 | 0.5 | 0.4 | 0.1 | <0.01 | <0.01 | 0.02 |
| Argentina | - | - | - | - | - | - | <0.01 | <0.01 | n.a. | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | <0.01 |
| Colombia | - | - | - | - | - | - | - | - | - | - | <0.01 | <0.01 | <0.01 | 0.01 | <0.01 | - | - | - | < 0.01 | <0.01 | <0.01 | <0.01 | 0.2 | 0.2 | 0.1 | ? |
| New Caledonia | 3.2 | 3.2 | 3.4 | 2.5 | 1.3 | 1.2 | 1.4 | 1.3 | 1.1 | 0.9 | 0.9 | 0.4 | 0.06 | - | - | - | 0.04 | | | | | | | | 0.01 | 0.1 |
| Sierra Leone | 0.6 | 0.7 | 0.7 | 0.6 | 0.6 | 0.5 | 0.3 | 0.4 | 0.5 | 0.1 | - | 0.3 | <0.01 | - | - | - | - | | | | | | | | | |
| Australia | 0.05 | 0.04 | 0.1 | 0.1 | - | 0.2 | 0.07 | 0.02 | <0.01 | 0.01 | - | 0.01 | - | <0.01 | <0.01 | - | - | | | | | | | | | |
| Bulgaria | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | | | | | | | | | |
| Roumania | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | | | | | | | | | |
| N. Vietnam | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | | | | | | | | | |
| Egypt | - | - | <0.01 | 0.02 | 0.02 | 0.01 | <0.01 | - | 0.01 | 0.01 | 0.03 | - | - | - | - | - | - | | | | | | | <0.01 | 0.01 | <0.01 |
| Guatemala | 0.04 | <0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.03 | 0.01 | <0.01 | <0.01 | <0.01 | - | - | - | - | - | | | | | | | | | |
| USA | 0.2 | 0.6 | 1.5 | 4.4 | 3.8 | 4.6 | 3.3 | 3.5 | 2.4 | 2.2 | 1.8 | - | - | - | - | - | - | | | | | | | | | |

Sources: Statistical Summary of the Mineral Industry 1960-1969, World Mineral Statistics 1970-76

TABLE 3. - World Chromite Production (Tonnes)

| Country | 1960 | 1961 | 1962 | 1963 | 1964 | 1965 | 1966 | 1967 | 1968 | 1969 | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S.Africa | 771907 | 897822 | 912743 | 792128 | 849510 | 942066 | 1060893 | 1149000 | 1152676 | 1197612 | 1427259 | 1644196 | 1483159 | 1649630 | 1876913 | 2075378 | 2409235 | 3318824 |
| USSR | 916000 | 920000 | 1148000 | 1229000 | 1320000 | 1420000 | 1420000 | 1520000 | 1646000 | 1700000 | 1750000 | 1800000 | 1850000 | 1900000 | 1950000 | 2080000 | 2100000 | 2180000 |
| Albania | 286004 | 234000 | 254000 | 293604 | 306808 | 310000 | 313000 | 326800 | 388000 | 429000 | 466000 | 502300 | 610000 | 611000 | 715000 | 779000 | 830000 | 880000 |
| Turkey | 479598 | 402711 | 469127 | 403871 | 412666 | 567036 | 511621 | 445783 | 418784 | 453881 | 518900 | 603200 | 680200 | 568500 | 666000 | 720000 | 710000 | 630000 |
| Rhodesia | 606340 | 536022 | 460547 | 374183 | 447558 | 635063 | 508000 | 317000 | 381000 | 363000 | 400000 | 400000 | 400000 | 550000 | 590000 | 590000 | 610000 | 608000 |
| Philippines | 734405 | 640272 | 531262 | 459100 | 468067 | 554496 | 560084 | 419734 | 438676 | 469636 | 566443 | 429584 | 349600 | 580268 | 529547 | 520038 | 431063 | 538299 |
| India | 106891 | 48783 | 66000 | 65039 | 34968 | 59682 | 77653 | 109530 | 205648 | 226056 | 273679 | 273135 | 281025 | 290537 | 396535 | 500294 | 402111 | 350698 |
| Madagascar | - | 10460 | 19300 | 11200 | 11769 | 2384 | - | - | - | 44773 | 104684 | 150000 | 111770 | 102500 | 155874 | 194127 | 211426 | 164789 |
| Finland | - | - | - | - | - | - | - | 6400 | 36200 | 71300 | 120509 | 112000 | 97000 | 147510 | 165479 | 331540 | 413981 | 593921 |
| Iran | 68000 | 73762 | 109700 | 97500 | 122000 | 132000 | 142000 | 149000 | 160000 | 183000 | 220000 | 200000 | 140000 | 140000 | 175000 | 155456 | 160000 | 165000 |
| Brazil | 5666 | 15455 | 24838 | 44038 | 25790 | 32048 | 24238 | 15025 | 17030 | 16071 | 34046 | 55969 | 70721 | 72824 | 88077 | 154465 | 132455 | |
| Cuba | 29730 | 24994 | 35600 | 55900 | 32500 | 29500 | 29500 | 29500 | 48513 | 45929 | 22836 | 13885 | 37104 | 37164 | 37734 | 38000 | 38000 | |
| Sudan | - | - | 8100 | 17300 | 17300 | 30500 | 17300 | 18300 | 22400 | 25400 | 47100 | 21000 | 23000 | 31548 | 24543 | 36578 | 23749 | 25000 |
| Japan | 67486 | 70168 | 58080 | 43729 | 43953 | 41832 | 32831 | 45209 | 27890 | 29781 | 32980 | 31642 | 24819 | 23174 | 28858 | 23149 | 22150 | 17986 |
| Cyprus | 20297 | 17981 | 6538 | 4908 | - | 4990 | 10618 | 21372 | 25103 | 23920 | 33335 | 40597 | 29644 | 29749 | 33809 | 27623 | 9156 | 14250 |
| Pakistan | 18384 | 25505 | 21473 | 14535 | 13503 | 14489 | 27145 | 26371 | 26020 | 26307 | 26032 | 30233 | 30683 | 20388 | 9479 | 9961 | 10872 | 12000 |
| Greece | 45689 | 77850 | 56245 | 51177 | 40097 | 47793 | 46326 | 10421 | 13200 | 24200 | 27440 | 14436 | 22130 | 18442 | 9589 | 24528 | 27000 | 30000 |
| Yugoslavia | 100577 | 108121 | 97040 | 93766 | 88354 | 79847 | 54209 | 47160 | 45259 | 39330 | 40565 | 34319 | 28137 | 6100 | 400 | 1700 | 2000 | 1500 |
| Argentina | | | | | | | | | | | | | | | | | 60 | |
| Colombia | - | 185 | 140 | 110 | 400 | 264 | - | - | - | 163 | 170 | 180 | 200 | 12000 | 12000 | 12000 | | |
| New Caledonia | 39159 | 36660 | 15454 | - | - | - | - | 1824 | - | - | - | - | - | - | - | 1050 | 9051 | 8310 |
| Sierra Leone | 5464 | - | 11449 | 2782 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Australia | 537 | - | 375 | 163 | 73 | 23 | - | - | - | - | - | - | - | - | - | - | - | - |
| Bulgaria | | | | ... | ... | ... | ... | | | | | | | | | | | |
| Roumania | | | | ... | ... | ... | ... | | | | | | | | | | | |
| N. Vietnam | | | | ... | ... | ... | ... | | | | | | | | | | | |
| Egypt | 300 | 1388 | - | - | - | - | - | - | - | - | - | - | - | - | 295 | 500 | 500 | 500 |
| Guatemala | 181 | 102 | 39 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | |
| USA | 96807 | 74000 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | |
| WORLD TOTAL (MILLION TONNES) | 4.40 | 4.22 | 4.31 | 4.05 | 4.24 | 4.90 | 4.83 | 4.66 | 5.38 | 5.36 | 6.11 | 6.36 | 6.27 | 6.79 | 7.57 | 8.28 | 8.55 | 9.46 |

**Sources:** Statistical Summary of the Mineral Industry 1960-1969, World Mineral Statistics 1970-76

TABLE 4. - World Reserves and Resources of Chromite Ore (million tonnes)

| Country | Reserves | % | Resources* Discovered | Resources* Undiscovered | Total | % |
|---|---|---|---|---|---|---|
| South Africa | 2270 | 66 | ? | ? | 8100 | 72 |
| Rhodesia | 1000 | 29 | 1100 | 510 | 2610 | 23 |
| USSR | 60 | 2 | ? | ? | 210 | 2 |
| Finland | 33 | 1 | ? | ? | 33 | 0.3 |
| India | 14 | 0.4 | ? | ? | 40 | 0.4 |
| Madagascar | 11 | 0.3 | ? | ? | 61 | 0.5 |
| Philippines | 3 | 0.1 | ? | ? | 19 | 0.2 |
| Turkey | 5 | 0.2 | ? | ? | 60 | 0.5 |
| Brazil | 7 | 0.2 | ? | ? | 18.2 | 0.2 |
| Albania | 6.5 | 0.2 | ? | ? | 21.5 | 0.2 |
| Iran | 5.0 | 0.2 | ? | ? | 45 | 0.4 |
| Cuba | 1 | <0.1 | ? | ? | 6 | 0.1 |
| Greece | 1 | <0.1 | ? | ? | 26 | 0.2 |
| Sudan | 1 | <0.1 | ? | ? | 1 | <0.1 |
| Yugoslavia | 0.5 | <0.1 | ? | ? | 0.5 | <0.1 |
| Japan | 0.5 | <0.1 | ? | ? | 1.5 | <0.1 |
| N. Vietnam | 0.5 | <0.1 | - | - | 0.5 | <0.1 |
| Cyprus | 0.2 | <0.1 | - | - | 0.2 | <0.1 |
| Pakistan | 0.2 | <0.1 | ? | ? | 2.2 | <0.1 |
| Colombia | 0.1 | <0.1 | - | - | 0.1 | <0.1 |
| Greenland | - | - | 10 | 10 + | 20 + | 0.2 |
| USA | - | - | 5.5 | 2.6 | 8.1 | 0.1 |
| Canada | - | - | 2.6 | 5.1 | 7.7 | 0.1 |
| Denmark | - | - | ? | ? | 2.5 | <0.1 |
| Australia | - | - | ? | ? | 2.0 | <0.1 |
| Sierra Leone | - | - | ? | ? | 1.5 | <0.1 |
| Togo | - | - | ? | ? | 0.5 | <0.1 |
| Afghanistan | - | - | ? | ? | 0.5 | <0.1 |
| Kenya | - | - | 0.1 | - | 0.1 | <0.1 |
| Total | 3419.5 | | | | 11298.6 | |

*The Reserves figures are also included in the columns 'Discovered' and 'Total' Resources.

Sources: USBM Mineral Commodity Summaries 1979
USBM Mineral Commodity Profiles - Chromium 1977
Reference 5
USGS Professional Paper 82, 1973
Geol. Survey of Greenland, Report 12, 39 p 1967

TABLE 5. - Theoretical Static and Dynamic Life of Reserves and Total Resources in the Main Producing Countries (with >2% of 1976 world production)

| | Theoretical life of reserves in Years | | | | Theoretical life of resources in Years | | | |
|---|---|---|---|---|---|---|---|---|
| | | Dynamic | | | | Dynamic | | |
| | Static | 2% | 4% | 6% | Static | 2% | 4% | 6% |
| South Africa | 942 | 150 | 93 | 69 | 3362 | 213 | 125 | 91 |
| Rhodesia | 1639 | 177 | 107 | 78 | 3557 | 216 | 126 | 92 |
| Finland | 79 | 48 | 36 | 30 | 79 | 48 | 36 | 30 |
| Madagascar | 52 | 36 | 28 | 24 | 288 | 96 | 64 | 49 |
| India | 34 | 26 | 22 | 19 | 99 | 55 | 40 | 33 |
| Brazil | 52 | 36 | 29 | 24 | 137 | 66 | 47 | 38 |
| USSR | 28 | 22 | 19 | 17 | 100 | 55 | 41 | 33 |
| Iran | 31 | 24 | 20 | 18 | 281 | 95 | 63 | 49 |
| Turkey | 7 | 6 | 6 | 6 | 84 | 50 | 37 | 31 |
| Philippines | 7 | 6 | 6 | 6 | 44 | 31 | 25 | 22 |
| Albania | 7 | 7 | 6 | 6 | 25 | 21 | 18 | 16 |

situation. To describe this in another way, at positive growth rates, reserves must be increased by very large proportions in order to bring about relatively small increases in theoretical reserve life. However, it is generally true that, in the past, mineral reserves have increased commensurately with increasing production.

### 2.1.3 Types of Chromite

Like any ore mineral, chromite may occur with gangue material which must be removed. Useful deposits may range in composition from 100% chromite down to 20% chromite. Deposits containing chromite exist in two quite different geological environments each of which has its influence on the exploration and extraction techniques that can be used. Chromite is used in three end-use sectors, each with different specifications. There are therefore three possible classifications of chromite; by chromium, aluminium and iron content, by ore deposit type, and by end use applicability. Quantitative information about chemical composition and ore deposit type is more easily available. The most useful classification, by end use applicability, is the most difficult for two reasons. The specifications of chromite regarded as acceptable for the three end uses have changed with time, and chromite from one geological deposit might be applicable to all, or only one, of the end uses. The three classifications are:-

#### 2.1.3.1 Chemical Composition and Gangue

The composition of run-of-mine chromite can vary in two fundamentally different ways. It may contain a certain proportion of silicate gangue minerals, the most common of which are olivine (Mg, Fe)$_2$ SiO$_4$, pyroxene (Mg, Fe) SiO$_3$, and their alteration products, serpentine $Mg_3Si_2O_5(OH)_4$ and magnetite $Fe_3O_4$. Feldspar $Ca(Al_2Si_2)O_8$ can also be found with chromite and is the main accompanying mineral in the Greenland deposits. It is possible to separate and reject most of the gangue materials by normal physical mineral processing.

Independently from this the composition of the chromite itself can also vary widely. For instance the $Cr_2O_3$ content may be between 33% and 55% of the total, The $Al_2O_3$ content between 9% and 30% and the Cr:Fe ratio can vary from less than 2:1 up to 4:1. This property of the chromite cannot be altered by normal physical beneficiation. Only by breaking down the lattice of chromite by chemical or metallurgical methods can the composition be altered.

As a first approximation, the chromium, iron and aluminium contents of the chromite are an indication of the use to which the product can be put. High chromium chromite is mainly used for metallurgical purposes, the high iron varieties mainly for chemical uses, although also significant in the other two sectors, and the high aluminium type for refractory purposes. (For more detailed specifications of each end use see 2.1.3.3.)

### 2.1.3.2 Deposit Type

Primary chromite deposits exist in two main forms:-

(i) Seamlike, stratiform ore bodies of the old shield regions such as South Africa, Rhodesia or Brazil. Seams can vary from several decimetres to several metres thick and may extend over 50 to 100 km in length with a silica content of only 10-20%. The composition of each seam remains constant over considerable distances and the chromite has characteristically high iron contents (16-25%) and low Cr/Fe ratios of 1.5-2.5. The contained chromite may be friable in nature, and the silicates cementing together the grains of chromite are often olivine or pyroxene.

(ii) Small lensoid or pod-like deposits of the type which occur for example, in Turkey, Albania, USSR, Iran. These ores are characteristically low in iron (10-12% FeO), high in chromium (46-60% $Cr_2O_3$) and have a high Cr/Fe ratio of 2.5-4.0. In most cases the ore bodies contain less than 10,000 tonnes of ore each and the largest discovered was the 1 million tonne Gololan deposit in Turkey, now worked out. Areas where several bodies exist in close proximity to give a total of hundreds of thousands to over 1 million tonnes of ore are not common. The contained chromite is unlikely to be friable and the associated gangue material is often the secondary minerals serpentine and magnetite.

From these characteristics it is clear that the stratiform deposits tend to be more iron-rich and have tended in the past to be used predominantly in the chemical sector. The podiform deposits are often chromium-rich and historically have been in great demand for metallurgical use. However, there are exceptions to this pattern (see 2.1.3.3).

The two deposit types have important differences with regard to two other processes relevant to their use. Exploration for deposits of the stratiform type is relatively easy. The geological environment is reasonably easily identified and continuous ore seams in any environment are relatively easily evaluated. Although the geological environment of the discrete pod-like chromite deposits is now well documented, understood and easily recognisable, the exploration for the contained chromite ores is much more difficult. At present there is no geophysical or geochemical method of exploration suitable for the identification of such bodies where they are buried to a depth of more than a few tens of metres. Only ore bodies at the surface or in-line with previous ore-bodies can be expected to be found. The successful separation of silicate material from the chromite is also dependent on type. Conventional mineral processing on stratiform chromite ores often produces clean fractures between the chromite and silicate. Often the ore is composed of equidimensional grains (Fig. 4) so loosely cemented that very little crushing/grinding is necessary to effect liberation of the chromite. The production of a concentrate with a low and predictable percentage of included silicate is therefore reasonably easy. Podiform chromite contains material with an in situ silicate content low enough to permit immediate use in lump form. Other ores need to be processed to remove silicates. However, each chromite grain is commonly fractured producing a much finer and irregular effective grain size (Fig. 5) cemented by a delicate and penetrative network of serpentine. The removal of this is difficult, not only because the ore needs to be ground to an extremely fine size in order to liberate the chromite, but also because the semi-plastic nature of the serpentine causes it to 'smear' over the particles of chromite. In those uses where the silica content of the product is important, e.g. refractory, and for certain chemical processes there may be a

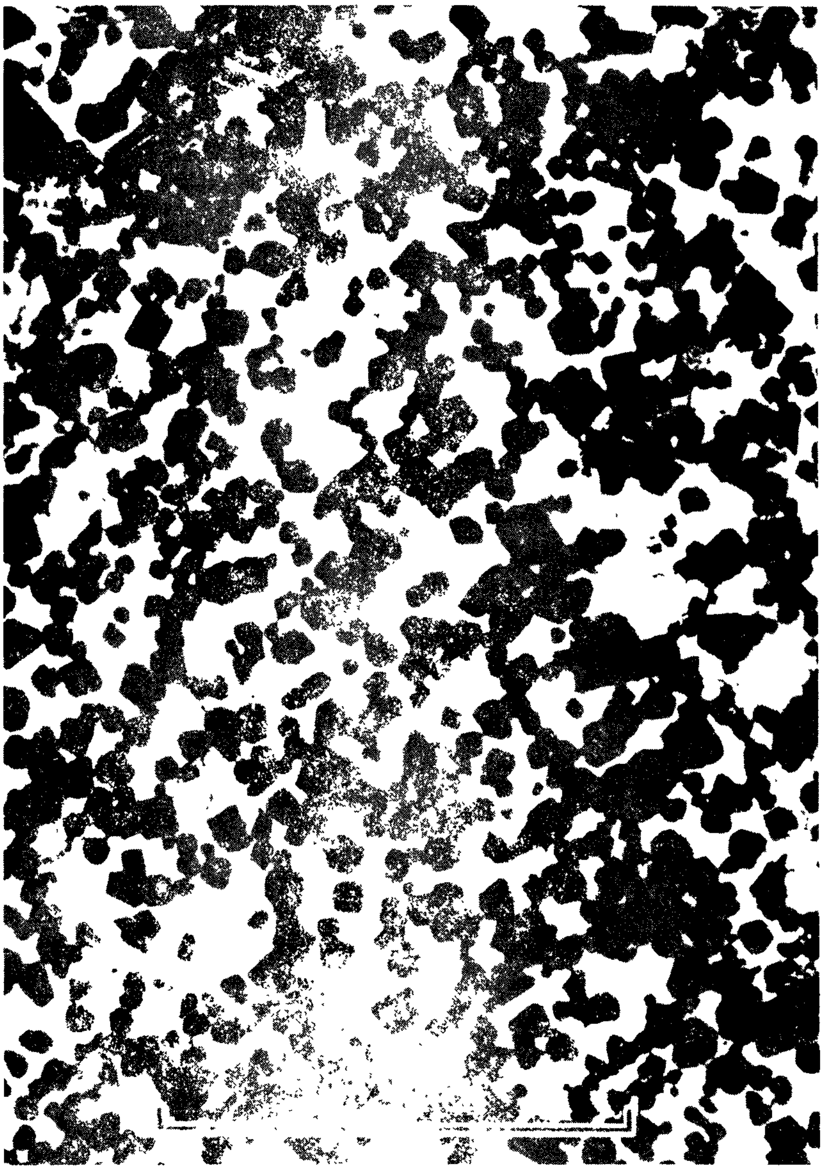

FIG. 4 STRATIFORM CHROMITE ORE. LOOSELY CEMENTED, SMALL, EQUIDIMENSIONAL CHROMITE GRAINS IN FELDSPAR AND PYROXENE GROUNDMASS. STILLWATER COMPLEX, MONTANA, U.S.A.

limit to the effectiveness of conventional mineral processing techniques for providing the desired product.

#### 2.1.3.3 End-Use Applicability

The classification of chromite into the three main use sectors 'metallurgical or ferro-alloys', 'chemical materials' and 'refractory materials' is no longer strictly applicable. However, it remains convenient for descriptive purposes:

(i) Metallurgical: It was the practice for buyers to specify a Cr/Fe ratio for chromite ore of not less than 2.8/1 and $Cr_2O_3$ greater than 48% in order that the ferrochromium produced should have a chromium content of at least 68%. This value was the minimum chromium content then acceptable to steel makers and chromite with these properties therefore became known as "metallurgical grade". There were also maximum permitted levels of 'fines' in the ore as higher percentage of these tended to produce difficult furnace operation due to uneven gas flow.

(ii) Chemical: Chromite ores used for chemical purposes should react well with soda ash, contain more than 45% $Cr_2O_3$ and levels of other elements that are not detrimental to the process used. That is, the consumption of chemicals used in any non-useful side reactions should be as low as possible. Normally $Al_2O_3$ and MgO contents should be as low as possible. The FeO contents should not be greater than 20% and the silica content less than 6%. Sulphur and some other elements (e.g. titanium, vanadium) should also be low and the Cr/Fe ratio of the ore should be about 1.6.

(iii) Refractory: Coarse-grained chromite is preferable with $Cr_2O_3$ + $Al_2O_3$ greater than 60% (31% $Cr_2O_3$ minimum). The ore should contain as much MgO as possible and as little iron as possible (12% Fe maximum). The associated non-oxide material should contain as little hydrated silicates as possible, the $SiO_2$ content should not exceed 6% and the $CaO/SiO_2$ ratio should be low. All these characteristics are concerned with restricting the formation of any low melting point compounds and therefore enhancing the refractory quality of the product.

A chromite sand for the foundry industry should have the following composition:-

$Cr_2O_3$ minimum 44%, total iron as $Fe_2O_3$ maximum 28%, $SiO_2$ maximum 4%, CaO maximum 0.5%.

The traditional requirement for low carbon ferrochromium (about 70% Cr) for metallurgical purposes, especially stainless steel making, has given way to an acceptance by steelmakers of material with a much lower specification, namely "charge chrome". Charge chrome generally contains only about 52% Cr and is high in carbon, but it is cheaper, and the steel maker receives the iron units free. The acceptance of this material by the industry was brought about by the coincidence of political and technical change - the application of sanctions to Rhodesian trade and the development of the Argon Oxygen Decarburisation (AOD) coverter which permitted the high carbon additions to be made without significant loss of chromium by oxidation. The result has been the development in South Africa of plants for producing charge chrome from the local relatively low Cr:Fe ratio chromite using indigenous coal. Makers of stainless steel tend now to reserve low-carbon ferrochromium only for final additions to the melt during the last stages of a blow. The trend towards the use of charge chrome therefore relieves the industry of its dependence upon deposits of the high Cr:Fe chromite which was essential to the production of the traditional ferrochromium.

The most important present requirement for both the chemical and refractory industries is a low silica content; a premium price is paid for very low $SiO_2$ contents, often lower than 3%.

### 2.1.4 World Reserves of Chromite by Chemical Composition

The recognition that not all the chemical varieties of chromite are interchangeable in the use to which they are put has given rise to a classification of world reserves and resources in terms of chemical composition (Table 6). Quite clearly this is not an accurate indicator of the amounts of chromite that could be available for

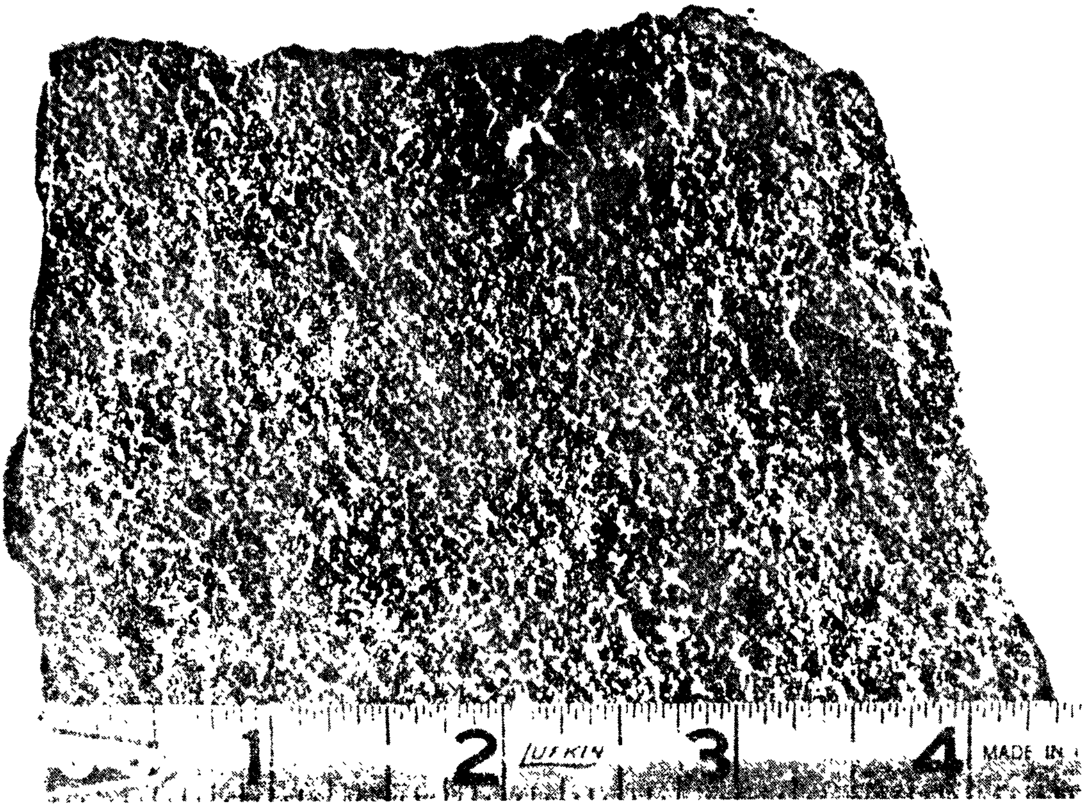

FIG. 5 PULL-APART TEXTURE IN CHROMITE ORE. FRACTURED GRAINS CEMENTED BY SERPENTINE GANGUE. (TREATED BY HF TO MAKE IT WHITE) TIEBAGHI MINE, NEW CALEDONIA.

TABLE 6. - Identified World Chromite Ore Resources* by Chemical Type
(Thousand short tons)

| Country | High chromium | | High iron | | High aluminium | |
|---|---|---|---|---|---|---|
| | Reserves | Other | Reserves | Other | Reserves | Other |
| Western Hemisphere | | | | | | |
| United States+ | | 400 | | 5 600 | ... | 100 |
| Brazil | 2 800 | 3 400 | 3 900 | 2 200 | 100 | 150 |
| Canada | ... | 100 | ... | 2 800 | ... | ... |
| Cuba | | 100 | ... | ... | 280 | 1 100 |
| Greenland | ... | ... | ... | 11 000 | ... | ... |
| Other | ... | 200 | ... | ... | ... | ... |
| Hemisphere total | 2 800 | 4 200 | 3 900 | 21 600 | 380 | 1 350 |
| Eastern Hemisphere | | | | | | |
| Finland | ... | ... | 11 000 | 5 600 | ... | ... |
| Greece | 50 | 50 | ... | 50 | 50 | 50 |
| India | 5 600 | 4 500 | 2 200 | 2 200 | ... | ... |
| Iran | 1 700 | 1 100 | ... | ... | ... | ... |
| Malagasy Republic | 4 500 | 3 400 | 1 100 | 2 200 | ... | ... |
| Philippines | 780 | 560 | ... | ... | 4 500 | 2 200 |
| South Africa | 56 000 | 56 000 | 1 100 000 | 2 200 000 | ... | ... |
| Southern Rhodesia | 560 000 | 560 000 | 56 000 | 56 000 | ... | ... |
| Turkey | 5 600 | 5 600 | ... | ... | ... | ... |
| USSR | 11 000 | 11 000 | 1 100 | 2 200 | 11 000 | 11 000 |
| Other | 1 100 | 1 100 | 1 100 | 1 100 | ... | ... |
| Hemisphere total | 646 330 | 643 310 | 1 172 500 | 2 269 350 | 15 550 | 13 250 |
| World total (rounded) | 650 000 | 650 000 | 1 200 000 | 2 300 000 | 16 000 | 15 000 |

* Mineral Facts and Problems 1975 USBM Bull. 667
(Derived from US Geological Survey Professional Paper 820, 1973)
\+ Submarginal resources not included

each end-use. Both Turkey and South Africa are credited with no high aluminium chromite resources and yet both countries market chromite for refractory purposes. Finland and Greenland are not credited with any high-chromium variety and yet their ores are respectively already used or have been considered for future use in the metallurgical sector.

If the classification based on chromium, iron and aluminium content is considered appropriate to metallurgical, chemical and refractory uses respectively then it is clear that there is an over-abundance of the high iron variety. The static life indices for resources of the high chromium, high iron and high aluminium varieties are about 200 years, nearly 2000 years and about 20 years respectively. This would suggest that the existing trends towards higher iron contents of chromite and ferrochromium for metallurgical use are likely to persist.

### 2.1.5 Possible Future Production

Prediction of future world supply and demand for chromite and the future trading pattern is beyond the scope of this report.

Conventionally, the ratio of the reserves figures for each country and the current production indicates the lifetime of the known reserves at current rates of output. However, active exploration for chromite deposits is taking place in many areas of the world; new deposits are being outlined e.g. Turkey, Brazil. More influential than complete exhaustion of all resources in a country is the element of cost competition. Those countries which exhaust higher grade deposits first will be faced with the decision of continuing production for foreign exchange reasons but at a commercial loss, or discontinuing production. The magnitude of the reserves in southern Africa (Table 4) theoretically allows production over a much longer period (Table 5) or increase in production rate. The advantages of the very large chromite ore deposits in South Africa, with relatively simple geological structure, are clear, and if the international market continues to be guided by normal market considerations then production will continue to be concentrated in that region. A significant shift in the balance of production would require a drastic increase in production rates from countries with smaller reserves or large new discoveries. The former is perhaps unlikely to result in the decrease in importance of the southern African production.

The chromite orebodies of the Republic of South Africa and of Rhodesia occur in the Bushveld Complex and the Great Dyke, respectively. The formation of these rock masses and the concentration within them of huge deposits of chromite appear to have been extremely unusual events in the geological history of the earth. Although future exploration may discover chromite deposits they are unlikely to be of the same order of magnitude of size as the southern African deposits and hence are unlikely to significantly alter the balance of production.

## 2.2 Chromium-Bearing Ferroalloys

### 2.2.1 Main Types Available

Ferrochromium and ferrosilico-chromium are the most important of the chromium intermediates used in the metallurgical industry. The main grades of the ferroalloys are:-

(i) Low-carbon ferrochromium: 63-73% chromium with a carbon content varying from 0.01-2.00%.

(ii) Medium-carbon ferrochromium: 60-65% chromium with a carbon content varying from 2.5-3.0%.

(iii) High-carbon ferrochromium: 60-72% chromium and a carbon content varying from 4-8%.

(v) Ferrosilico-chromium: ferrochromium with a low chromium content 35-55%, 25-45% silicon and up to 1% carbon.

The chromium and carbon contents are two important chemical variables in the range of ferrochromium produced. The chromium content is mainly dependent on the Cr/Fe ratio of the ore or blend of ores used as both the iron and chromium are reduced in the furnace. In general, the higher the carbon content of the product the cheaper the costs of the manufacturing process and the lower the price.

### 2.2.2 Geographical Distribution of Production

Both ferrochromium and ferrosilico-chromium are produced in over 20 countries. The market competition in ferroalloys has been severe in the past few years with many producers switching furnaces to the production of more profitable ferroalloys. Because of secrecy within the ferroalloy industry current capacities for all producers are not available. Table 7 is an estimate of the production capacity of major producers of chromium-bearing ferroalloys.

TABLE 7. - Plant capacity by country for chromium-bearing ferroalloys 1978

| | '000 tonnes | % |
|---|---|---|
| Federal Republic of Germany | 200 | 7 |
| France | 147 | 5 |
| Italy | 55 | 2 |
| Total EEC | 402 | 14 |
| Finland | 50 | 2 |
| Norway | 40 | 1 |
| Sweden | 326 | 11 |
| Total EFTA | 416 | 14 |
| Spain | 38 | 1 |
| Yugoslavia | 93 | 3 |
| EUROPE EXCLUDING EASTERN BLOC | 949 | 33 |
| Canada | 50 | 2 |
| USA | 390 | 13 |
| North America | 440 | 15 |
| Mexico | 6 | <1 |
| Brazil | 102 | 4 |
| Argentina | n.a. | n.a. |
| Latin America | 108 | 4 |
| Republic of South Africa | 365 | 13 |
| Rhodesia | 230 | 8 |
| Africa | 595 | 20 |
| Turkey | 65 | 2 |
| India | 30 | 1 |
| Japan | 717 | 25 |
| Asia excluding Eastern bloc | 812 | 28 |
| Australia | n.a. | n.a. |
| Philippines | 2 | - |
| TOTAL WESTERN WORLD | 2906 | 100 |

Sources Reference 5
Ferroalloys: a world survey. Metal Bulletin 1979

### 2.2.3 Changes in Type of Ferroalloy and Geographical Distribution of Production with Time

During the last decade the use of a high carbon ferrochromium by the steel industry has increased considerably whereas the consumption of low carbon ferrochromium has remained constant or declined. This is a consequence of the introduction of the AOD process which permits the use of higher carbon ferrochrome in the stainless steel converter. The introduction of argon and oxygen allows the steel to be decarbonised without oxidation, and consequent loss of chromium because of the low partial pressure of the oxygen in the melt.

Low-carbon ferrochromium is now necessary predominantly for final adjustment to the special steel or alloy melt and for the preparation of tailor-made special alloys in the induction furnace. The future demand for low-carbon ferrochromium is expected to be limited in view of the possibilities of using the cheaper high-carbon ferroalloys.

The technical improvements which permitted the use of higher carbon ferrochromium in the steel industry coincided with a period of short supply of high-chromium chromite. The introduction of 'charge chrome', by the South Africans made their very large reserves of high-iron chromite available for metallurgical use and helped to alleviate the problem. As the Transvaal ore is friable, the difficulties of using this in the ferroalloy furnace had to be met by pelletising or briquetting. Customers have become used to the lower chromium contents, cheaper prices and the bonus of free high grade iron.

The probable changes in the balance of chromium ferroalloy production capacities for certain geographic units are shown in Table 8.

TABLE 8. - Chromium Bearing Ferroalloy Production Capacities (in percentage of total)

| Geographic Unit | High-carbon Ferrochromium | | Lower-carbon Ferrochromium | | Ferrochrome silicon | |
|---|---|---|---|---|---|---|
| | 1977 | 1985 | 1977 | 1985 | 1977 | 1985 |
| USA and Canada | 13.6 | 11.7 | 12.6 | 12.9 | 23.0 | 31.1 |
| Total Europe | 17.1 | 16.1 | 50.8 | 44.0 | 44.3 | 36.5 |
| Rhodesia and South Africa | 47.4 | 50.9 | 21.8 | 30.1 | 19.8 | 20.6 |
| Japan and rest Western World | 21.9 | 21.3 | 14.8 | 20.2 | 12.9 | 11.8 |

Source: McFarlane. Metal Bulletin's First International Ferro-Alloys Conference 1977.

One of the most important factors with regard to Europe is that unless new high-carbon ferrochromium plants are built the production capacity will only meet 37% of the requirements. In line with the decline in importance of low-carbon ferrochromium, the world capacity was expected to fall by 40-50% between 1977 and 1985. To 1985 the total world ferrosilico-chromium requirements and the balance of production are not expected to change.

With regard to changes in the distribution of chromium ferroalloy production in the long term, a domestic supply of chromite, solid furnace reductant and cheap electricity favours the introduction of plant. For one or other or a combination of reasons, countries in a favourable position probably include South Africa, Rhodesia, Brazil, Finland and Turkey. On this basis, the outlook for ferroalloy production in Japan, North America and Europe is unfavourable.

## TABLE 9. - Direct Import Dependence of EEC Countries on Supplies of Chromium, Calculated on Cr Content Basis (1978)

| UK | % | Belgium-Luxembourg | % | Denmark | % | France | % | Germany FR | % | Irish Republic | % | Italy | % | Netherlands | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| South Africa | 55 | Sweden | 25 | Germany FR | 45 | South Africa | 26 | South Africa | 59 | n.a. | | South Africa | 28 | South Africa | 49 |
| Sweden | 13 | Soviet Union | 23 | Sweden | 40 | Madagascar | 22 | Sweden | 10 | | | Turkey | 22 | Mozambique | 18 |
| Norway | 6 | Finland | 12 | Norway | 4 | Turkey | 14 | Soviet Union | 8 | | | Sweden | 16 | Germany FR | 16 |
| Philippines | 5 | Germany FR | 11 | | | Iran | 9 | Finland | 6 | | | Yugoslavia | 9 | Finland | 7 |
| Soviet Union | 3 | Unspecified | 22 | | | Soviet Union | 7 | Turkey | 4 | | | Albania | 7 | Soviet Union | 4 |
| Mozambique | 3 | | | | | Finland | 6 | | | | | Soviet Union | 2 | | |
| | | | | | | Sweden | 5 | | | | | France | 2 | | |
| | | | | | | | | | | | | Unspecified | 6 | | |

### Aggregate of EEC Countries Derived From Above

| | % |
|---|---|
| South Africa | 44 |
| Sweden | 11 |
| Turkey | 9 |
| Soviet Union | 6 |
| Finland | 5 |
| Madagascar | 4 |
| Iran | 3 |
| Albania | 2 |
| Germany FR | 2 |

### Total Direct Import Dependence of EEC Countries on Supplies From Outside EEC

| | % |
|---|---|
| South Africa | 46 |
| Sweden | 11 |
| Turkey | 9 |
| Soviet Union | 6 |
| Finland | 5 |
| Madagascar | 5 |
| Iran | 3 |
| Albania | 2 |
| Yugoslavia | 2 |

## 2.3 Possible Supply Problems

### 2.3.1 General

Supply problems for any mineral raw material may result from changes in the pattern of supply (producer effect) and the interaction of this with the acquisition policy of the consuming country.

Producer effects include strikes, accidents in mines, political disturbances, inadequate investment in plant and exhaustion of ore. Short strikes and minor disruption of mine production can be alleviated by drawing on stockpiles. Longer strikes, more severe accidents or inadequate production capacity may cause general shortages and price rises. Raw material exhaustion may be real and unavoidable at prevailing prices or gradually come about because of insufficient investment in exploration. The relevance of theoretical life indices of the major producing countries to the changing pattern of production has already been discussed. In this content the long term advantages of South Africa and Rhodesia are clear.

### 2.3.2 Community Supplies

#### 2.3.2.1 Dependence of the Community on Supplies of Chromium in all Forms

The dependence of the Community on certain countries for supplies of chromium-bearing materials can be illustrated in a number of ways. Table 9 shows the proportions of contained chromium imported in to Community countries from the main supplying countries upon which the Community is dependent. More useful, perhaps, as an indication of vulnerability is the concept of indirect dependence, i.e. the degree to which consumers are dependent on the exporters of chromite rather than intermediates. For example, countries importing Norwegian ferrochrome are thereby indirectly dependent on South African chromite which is imported by Norway for ferrochrome production.

The high direct dependence of the Community on supplies from South Africa is evident from trade statistics. However, its indirect dependence is much greater.

#### 2.3.2.2 Dependence of the Community on Chromium in Specific Form

Shortages, not of chromium units, but of chromium in one or several related forms can occur due to excessive dependence on one supplier of a particular form. The import dependence of the Community on a limited number of countries affects at least the ferroalloys, ores and concentrates (Table 10).

TABLE 10. - Direct Import Dependence of the Community on Supplies of Different Chromium-Bearing Materials in 1977

| | Ferro-chromium % | Ferrosilico-chromium % | Ores and concentrates % |
|---|---|---|---|
| South Africa + Mozambique | 46 | 45 | 51 |
| Scandinavia | 22 | 18 | 1 |
| USSR | 4 | - | 10 |
| Turkey | 1 | - | 15 |
| Madagascar | - | - | 7 |
| Others | 13 | 15 | 15 |
| Total Non-EEC | 86 | 78 | 99 |

The increasing trends towards trade in ferroalloys as opposed to trade in chromite, and towards concentration of ferroalloy production in countries with substantial chromite reserves, are likely to intensify the vulnerability of major consuming countries without indigenous chromite.

## 3. USES OF CHROMIUM

The uses of chromium are normally classified as metallurgical, refractory and chemical. Only a small proportion of consumption is in the form of chromium metal- this is used in the manufacture of high-performance alloys such as superalloys where high purity is important. The chromium content of steel alloys is supplied in the form of ferroalloys or, to a substantial extent, by the recycling of steel scrap. Chromite ore is used directly in the foundry industry and, in combination with magnesite, for the manufacture of refractory bricks. Chromite is also the starting point for the manufacture of sodium dichromate, from which a wide range of chemicals is made for use in electroplating, leather tanning, pigments, wood preservatives etc. The most important applications of chromium are summarised in Fig. 6.

### 3.1 Metallurgical Uses

Chromium is used as an alloying constituent in commercial metal products to confer strength, hardenability, and resistance to wet corrosion and high temperature oxidation. Its presence is also important to modify structure and ensure long-term stability in alloys. It is also used as coatings for corrosion resistance, for hardfacing and for decorative purposes, but these applications are considered in Section 3.3.1. Stainless steels represent the biggest single end use of chromium and will be discussed first, followed by brief descriptions of the other metallurgical applications, many of which are very important although the consumption of chromium is relatively small.

### 3.1.1 Stainless Steels

The development of stainless steels dates back to 1912-13, when the austenitic alloys containing 18-20% chromium and 8-10% nickel were formulated at the Krupp works and the martensitic steel containing 13% chromium was introduced in Great Britain. It was known at this time that the presence of 12-13% chromium conferred superior resistance to both wet corrosion and high-temperature oxidation. Although further increases were beneficial, the maximum degree of resistance in some environments being reached at 35% or even 50% chromium, the austenitic steels had excellent properties for many purposes, with an ease of working which made them eminently suitable for a wide range of applications. Development of stainless steels has been determined largely by the physical metallurgy of the iron/chromium/nickel system, because the possibility of hardening the alloys by heat-treatment depends on the opposing effects of chromium and nickel on the stability of the austenite phase, given the greater solubility of carbon in the latter. This has led to the emergence of three groups of stainless steels differing in chromium content and hence in resistance to chemical attack, and also in their mechanical properties, not all the desirable combinations of these properties being obtainable. The three groups are as follows:

#### Martensitic steels

These can be hardened and tempered to varying degrees according to the carbon content in much the same way as for plain carbon steels. Their resistance to corrosion is not of the highest class, although it is adequate for many purposes. Steels containing up to 18% chromium can be made heat-treatable by including some nickel or by increasing the carbon content, and these have better resistance to corrosion than the usual 12-14% chromium martensitics.

#### Ferritic steels

These are not heat-treatable, but their resistance to oxidation and corrosion is high, though not so good as for the austenitic grades of similar

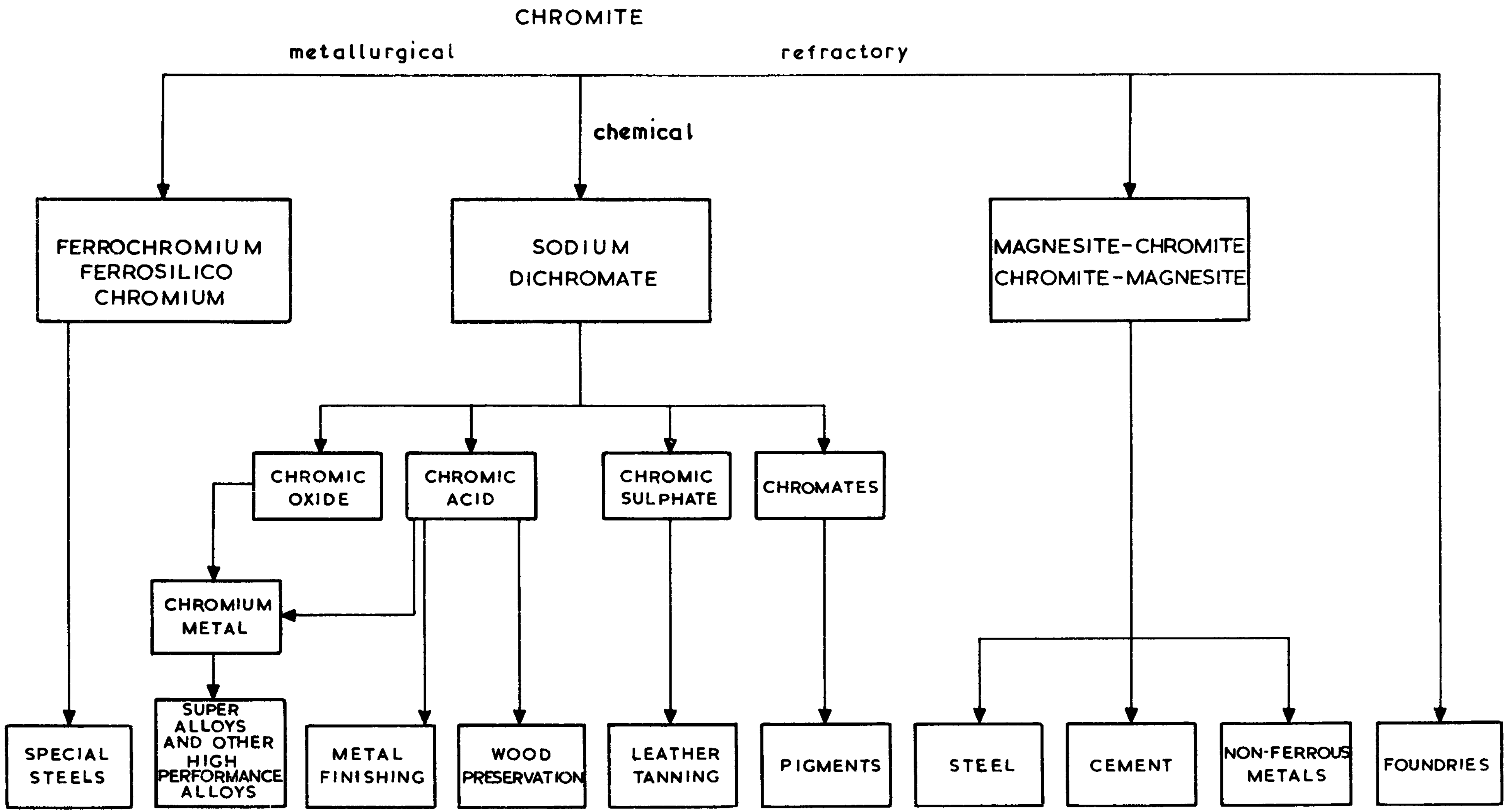

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**FIG. 6** END-USES OF CHROMIUM

chromium content. The chromium content is usually 16-18%, but may be as high as 27%. Their mechanical strength may be affected by grain-coarsening, and by the formation of chromium-rich precipitates.

Austenitic steels

These contain chromium, usually 18-20%, with sufficient nickel (usually about 8%) to maintain a fully austenitic structure. They are therefore not hardenable by heat- treatment, although they can be usefully strengthened by cold deformation. Resistance to wet corrosion and high-temperature oxidation is outstanding, but they are susceptible to stress-corrosion cracking. Workability is good, and they are particularly suitable for deep drawing. High-temperature creep strength is greater than for the ferritic materials.

This was the position reached in the 1920's, since when development has taken the form largely of seeking more highly resistant materials for special purposes, by increasing contents of chromium and nickel, by minor additions, particularly of silicon aluminium and molybdenum, and by adjusting the contents of such elements as carbon and nitrogen. These developments usually involve relatively minor modifications to composition to optimise weldability, or resistance to some particularly corrosive liquid.

Several sub-categories of stainless steel have appeared, e.g. the precipitation-hardenable steels, with particularly desirable properties for some special application, but which usually demand close control of composition, and may sacrifice workability or long-term metallurgical stability in the interest of securing some other advantage.

Generally speaking these materials can be divided into conventional stainless steels containing 12-20% chromium, and the high-performance alloys containing up to 50% chromium. The first group includes ferritic and martensitic compositions as well as the ubiquitous austenitics. On the whole, the austenitic steels are considerably superior to the others in corrosion resistance, high-temperature strength and formability, but they are more expensive because of their relatively high nickel content. Certain grades containing molybdenum are particularly useful because of their resistance to pitting corrosion in a number of environments. The ferritic grades offer reasonably good corrosion resistance at comparatively low cost and are less susceptible to stress corrosion cracking. The cheapest materials are the heat treatable martensitic steels which combine high mechanical strength with moderate resistance to corrosion.

The selection of stainless steels for industrial purposes is influenced by a wide variety of considerations, by no means all of which are technical. Appearance, ease of cleaning, prestige, and ready availability in a suitable form appear to be at least as important as prices, since it is often possible to recoup a considerable increase in the cost of materials if the customer appeal is enhanced. Once a material has become available, its use will be readily extended into areas where not all of its superior properties may be needed. Apart from this, the technical properties may themselves be over-specified for the sake of reliability or appearance. Since the price of a given grade of steel depends on the size of the market as well as on the cost of the basic materials, market forces may act against efficient specification and there has been a decided tendency to reduce the number of grades of steel in production. The dominant position of Type 304 steel in the market reflects the fact that it is a material with excellent all-round properties which is available in a very wide variety of forms because of its high workability, and the comparatively high cost imposed by its nickel content does not prevent its being used in many consumer applications where many of its properties are not really required. This situation does, however, owe a good deal to the fact that, since it can easily be produced in thin sections of complex shape the quantity of material needed may be very small, for instance, in decorative applications.

End-uses of stainless steels are very diverse, ranging from consumer goods such as razor blades, furniture and kitchen equipment right up to heavy plant for the chemical industry and power generation. Table 11 gives the compositions of a number of grades of stainless steel in common use, with brief notes on properties and applications.

TABLE 11. - Commercial Stainless Steels

| AISI type no. | Fe | Cr | Ni | Al | Mo | Mn | C | N | Others | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| Martensitic | | | | | | | | | | |
| 410 | bal. | 11.5-13 | - | - | - | 1.0 | 0.15 max | - | Si 1% max | Low-cost heat-treatable steel for cutlery etc. |
| 431 | bal. | 15-17 | 1.2-2.5 | - | - | 1.0 | 0.2 max | - | Si 1% max | High mechanical properties |
| 440C | bal. | 16-18 | - | - | 0.75 max | 1.0 | 0.95-1.2 | - | Si 1% max | High strength, corrosion resistant. Used for instruments and valves |
| Ferritic | | | | | | | | | | |
| 409 | bal. | 10.5-11.75 | - | - | - | 1.0 | 0.08 | - | Si 1% max<br>Ti 6x%C | Low-cost steel for exhaust systems. Resists embrittlement |
| 430 | bal. | 16-18 | - | - | - | 1.25 | 0.12 max | - | - | High formability. Used for car trim and chemical equipment |
| 446 | bal. | 23-27 | - | - | - | 1.5 | 0.2 max | 0.25 max | - | High corrosion resistance |
| 406 (Fecralloy) | bal. | 15 | - | 4 | - | - | - | - | Fecralloy 1%Y | Oxidation resistant; low mechanical strength |
| Kanthal | bal. | 23 | - | 5.7 | - | - | 0.06 | 0 | 2% Co | High temperature electric resistance heaters |
| Austenitic | | | | | | | | | | |
| 304 | bal. | 18-20 | 8-12 | - | - | 2 | 0.08 max | - | Si 1% max | General-purpose corrosion-resistant steel: high formability |
| 316 | bal. | 16-18 | 10-14 | - | 2-3 | 2 | 0.08 max | - | Si 1% max | Corrosion resistant: used for chemical plant |
| 347 | bal. | 17-19 | 9-13 | - | - | 2 | 0.08 max | - | Nb+Ta 10x%C | Resistant to weld decay: chemical engineering |
| 310 | bal. | 24-26 | 19-22 | - | - | 2 | 0.25 max | - | - | Furnace hardware, reformers |

### 3.1.2 Engineering Steels

The main attribute of chromium in low alloy steels is its effect on hardenability and toughness, especially when used in conjunction with other elements. It increases resistance to corrosion and abrasion, and slightly increases strength at elevated temperatures. Chromium contents average about 2%, but may be as high as 9%.

High strength low alloy steels were developed primarily to obtain improved strength-to-weight ratios in order to reduce the dead weight of transportation equipment. There followed the development of heat treated structural steels of still higher strength-to-weight ratio with no loss of weldability or fabrication properties. One of the most recent high growth areas in HSLA steels has been for pipelines for the transmission of gas or oil. Engineering steels also include wrought steels used for gears, rollers etc, cast steels for railway truck components, the chromium/molybdenum steels used extensively in steam turbines, and some heat-resisting materials.

### 3.1.3 Tool Steels

Tool steels comprise materials for cutting tools (e.g. drills), dies, extrusion tools and press tools for drawing etc. High-speed steels generally contain 4% chromium, cold-work die steels contain 12% chromium, while hot-work die steels contain up to 5.5% chromium.

### 3.1.4 High Performance Alloys

The term high performance alloy is used here to indicate special iron, cobalt or nickel based alloys, many of which contain chromium and which withstand extreme conditions of heat, wear, and corrosion. The most important groups are nickel-based and cobalt-based superalloys and special iron-nickel or nickel-based alloys for chemical plant and electrical resistance heaters. The first two, accounting for about one third of the total in terms of chromium demand, are used mainly for gas-turbine power blading. Chromium is essential for resistance to high-temperature oxidation and corrosion, and also plays an important part in a complex set of strengthening mechanisms. Nearly all nickel-based and cobalt-based superalloys contain chromium at levels varying from 5-30%.

The stellite cobalt-based alloys, and the nickel and iron-based casting and hard-facing alloys contain chromium in proportions ranging up to 35%.

The other main group of alloys in this category are Inconel (used in heat-treatment and furnace equipment, chemical and food processing plant) and electrical resistance materials.

### 3.1.5 Cast Iron

The resistance to wet corrosion and low stress abrasion and erosion is important to many mineral processing and allied operations. The use of cast iron with 12-20% contained chromium as well as small quantities of other elements such as copper, nickel and molybdenum increases the life of exposed components. Some of the more important uses are dry grinding of cement in ball mills, milling of coal for power stations, dies for brick-making and briquetting, and equipment for grinding, mixing and classification of ores.

## 3.2 Refractories

Chromite was first used as a refractory material in the late 19th century to prevent reaction at junctions between acidic (e.g. silica or fireclay) and basic (e.g. dolomite or magnesite) refractories. It came to be used on a large scale when fired bricks containing both chromite and magnesite were found to give improved resistance to thermal shock. Chromium-bearing refractories are used in bricks and cements in the metallurgical, glass and cement industries, and in foundry sand. Bricks are described as chromite-magnesite if the chromite content exceeds 50%, and otherwise as magnesite-chromite.

### 3.2.1 Refractory Bricks

Fired bricks have now largely superseded chemically bonded materials. Originally they possessed rather poor refractoriness and resistance to slags, because they contained a silicate bonding phase derived from impurities in the raw materials, but improved types are now made from high-purity magnesite extracted from seawater. Since 1970, co-clinkered magnesite-chromite bricks have captured a large share of the market in spite of their higher price. Fusion-cast magnesite-chromite bricks of high density are still more expensive, but are used in exceptionally severe environments. Table 12 compares prices of a number of refractory materials.

TABLE 12. - UK Prices of Some Refractories

| Type of brick | Price, £/tonne |
|---|---|
| Directly bonded magnesite-chrome | 250-260 |
| Co-clinkered magnesite-chrome | 350-360 |
| High-purity magnesite | 350-360 |
| Fire-bonded dolomite | 160-180 |
| Tar-bonded dolomite | 140 |

About 70-75% of all refractory products are used by the iron and steel industry; other industries (cement, glass, non-ferrous metals etc) each account for less than 5% of the total, either because the industry is itself small, or because little refractory is consumed per unit of output. An excellent review of trends in refractories is given by Spencer[1].

#### 3.2.1.1 The Steel Industry

The open-hearth (Siemens-Martin) furnace was the major outlet for chromite-magnesite bricks, but this process is now obsolescent. Electric-arc furnaces now constitute the most important application for chromite-bearing refractories. Even here, most of the magnesite-chromite bricks now used could if necessary be replaced by magnesite; although the latter may have low resistance to thermal shock, this can be improved by modern methods of manufacture. Much of the cost of operating an arc furnace is associated with maintenance of the refractory lining, and down-time has a major effect on unit costs. For this reason, high-purity magnesite bricks are now preferred to magnesite-chromite for high-wear areas, and particularly below the slag-line. Use of chromite is also declining through the introduction of water-cooled panels in furnace sidewalls. Approximately 70% of the wall area is occupied by water-cooled elements, virtually eliminating conventional refractory brickwork from the upper part of the furnace wall i.e. above the slagline, in the area where magnesite-chromite is normally used. There is some controversy about the cost-effectiveness of this method, but its value appears to have been accepted in high output furnaces. In the UK it is expected that most big arc furnaces will be converted to water-cooling during the next two years.

Arc furnace roofs are usually lined with high-alumina bricks, although these may be short lived if the furnace is driven hard. There has been a tendency to substitute magnesite-chromite bricks for better resistance to slag attack, but the full potential benefit is not obtained because of distortion under thermal stress, which makes it necessary to support the roof. In some cases unsupported roofs with cheap reclaimed magnesite-chromite bricks are used, but the availability of reclaimed materials is decreasing in the UK. The trend towards increased usage of magnesite-chromite for this application has not progressed very far, and may even decline if the market for steel revives, because water-cooling may well then be extended to arc furnace roofs.

Dolomite bricks have to a large extent superseded the more expensive magnesite-chromite for lining the argon-oxygen furnaces which now dominate secondary steelmaking. Refractory lives are usually similar for the two materials, although in some cases dolomite may last twice as long. Small quantities of magnesite-chromite are used in ladles, especially where the slag contains silica. In most cases magnesite would be satisfactory, and indeed has to be used in situations where chromium uptake might contaminate the steel.

#### 3.2.1.2 Rotary Kilns

Cement kilns traditionally used aluminosilicate refractories in the burning zone, but changed to magnesite-chromite as conditions became more severe. However, with the trend towards bigger kilns it has been found that fired dolomite gives better performance, and 50% of magnesite chromite has been replaced. If magnesite-chromite were not available there would be even greater usage of dolomite. Magnesite could be used, at greater cost, or a magnesium aluminate spinel.

Other rotary kilns, such as those used in lime and dolomite burning, are lined with magnesite-chromite. Consumption is of the same order as in secondary steelmaking. Firing temperatures are higher than in cement kilns (up to 2000°C compared with 500°C).

#### 3.2.1.3 Other Users of Chromite Refractories

The non-ferrous metal industry provides a very stable market for magnesite-chromite because the slags in the smelting of copper, lead and nickel are highly silicious and no completely satisfactory alternative refractory is available.

Small quantities of chromite are used in the glass industry, mainly in the heat exchangers, but on the whole this industry avoids chromite because of the dangers of discolouration of the product.

A new development is the use of chemical grade chromic oxide, rather than chromite ore, in conjunction with alumina as a refractory material. Consumption in the UK is still very small, but large tonnages are sold in the USA and Japan. The steel industry is becoming interested in these refractories for high wear parts of furnaces, in order to reduce down-time. They are also used in the production of fibreglass because of the highly corrosive conditions which prevail.

### 3.2.2 Foundry Sands

Refractory sands, such as chromite, zircon and olivine, are widely used in steel foundries. These sands offer a number of advantages over silica sands, including lower reactivity with metal oxides during the casting process, lower thermal expansion and higher resistance to metal penetration. Refractory sands are relatively expensive, and it is common practice to apply them as facings to silica sand.

The usefulness of chromite as a moulding material was first recognised in South Africa, where its successful application in the production of austenitic manganese-steel castings was demonstrated[2]. Considerable investigatory work followed in other countries, and as a result chromite sand has become established as a steel foundry moulding material in all industrial countries. The best chromite sands are produced from the Transvaal ores, but Finnish chromite sands are also available. Foundry sands are produced by crushing the ore, washing to remove impurities and gangue minerals, and then screening to give the desired gradings. The $Cr_2O_3$ content should be higher than 44%, and the sand should contain low proportions of lime and silica. Hydrous minerals such as serpentine are undesirable because evolution of combined moisture may lead to blowhole defects in the casting.

It is generally accepted that chromite sand offers higher resistance to penetration by molten steel than do zircon or fine silica sands. Steel castings exceeding 100 tonnes in weight have been made very successfully using mould and core facings of chromite sand, and a first class surface finish is usually achieved. The major problem which occurs from time to time is known among foundrymen as chromite sand disease. This is a burn-on type of defect for which there appears to be no easy cure.

The problem occurs sporadically and is associated with variability in composition of chromite sands and the presence of impurities which affect their finer characteristics. Some foundries prefer to use a mixture of chromite and zircon to avoid such defects.

## 3.3 Chemical Applications

The basic process in the chromium chemicals industry is the manufacture of sodium dichromate. In order to release the chromium from the chromite lattice the chemical grade ore is first roasted with nearly stoichimetric proportions of sodium carbonate (soda ash) and extracted with water to yield sodium chromate solution. This is then converted to the principal chromium chemical, sodium dichromate, by acidifying with sulphuric acid or carbon dioxide. Most chromium chemicals are made from a sodium dichromate starting point and there are important world producers within the Community (Bayer in Germany, Stoppani in Italy, British Chrome and Chemicals in the UK).

The most important secondary products are:

1. Chromic oxide $Cr_2O_3$ The main outlet is for production of chromium metal by the alumino-thermic route for manufacture of high temperature alloys. Other outlets include pigments and the new $Cr_2O_3$ refractories.

2. Chromic acid This is used mainly in decorative and hard chromium plating, for which the markets are of approximately equal size. It is also used in the manufacture of copper - chromium - arsenic timber preservatives.

3. Basic chromium sulphate $Cr(OH)SO_4$ This is produced entirely for the leather tanning industry.

4. Pigments Sodium dichromate is used to produce lead, zinc and other chromate pigments which are widely used in paints.

The above uses each account for a few per cent of chromium consumption. Other applications which use relatively small amounts include chromium lignosulphonate drilling mud additives, corrosion inhibitors for closed systems, catalysts and magnetic tapes.

Although individual chemical applications of chromium account for only a small proportion of consumption, wastage rates are high and there is concern about the high toxicity of hexavalent chromium. There is therefore a case to be made for recycling in some cases. This topic is pursued in Chapter 5.

### 3.3.1 Metal Finishing

Chromium is a constituent, often the major one, of coatings for decoration or corrosion protection, for resistance to high-temperature oxidation or mechanical wear, and for restoring worn parts. In these applications a relatively small quantity of chromium plays an important part in material conservation by making cheap and abundant metals perform functions for which their properties would otherwise be inadequate.

Electroplating is the most important method used to apply coatings of chromium, and the technology is described in some detail below to provide a basis for understanding the potential for chromium conservation in this industry. For high temperature use, chromising is the principal method of obtaining a chromium-rich surface on steel. It is a diffusion process which produces an effective stainless steel surface with a mean chromium content of about 35%. This is an effective method of improving the corrosion resistance of mild steel in applications such as car exhausts and heat exchangers, but the process tends to be expensive and does not offer strong competition for stainless steel in most applications. Other surface processes using chromium include sputtering, ion implantation, chemical vapour deposition, plasma-spray coating, cladding and weld overlay coating. Only the latter two have much commercial significance at the present time. Like chromising, the use of these techniques could conserve chromium, but their adoption depends upon the relative economics of using solid stainless steel or a surface coating.

Other metal finishing processes which use chromium chemicals include passivation and chemical conversion coatings. In the former dipping in chromic acid solution produces an oxide film on aluminium or galvanised iron. Conversion coatings are gel-like structures produced when a non-ferrous metal (e.g. magnesium, aluminium, zinc, cadmium) is immersed in chromate solution. They can be formed in a variety of colours and form a satisfactory base for paint.

### 3.3.1.1 Electroplating

There are two types of chromium plating:

(i) Decorative plating, which consists of a relatively thin layer, 0.3-0.5 μm, on an undercoat of nickel. It is used mainly in the consumer goods industries such as cars, bicycles and domestic appliances.

(ii) Hard chromium plating, which consists of a thick layer of chromium, (20-200 μm), on engineering components frequently made of hardened steel. Unless a very thick protective layer is required there is usually no underlayer of nickel. The hard plating applications are more common in industrial equipment, for instance in the chemical and food industry, the printing industry and the paper industry.

The electrolytes used for decorative plating consist of chromic acid containing sulphate ions as a catalyst. The concentration of chromic acid in the bath is not critical, and is normally in the range 150-550 g/l. The ratio of chromic acid to sulphuric acid, however, is most important and is normally in the range 80:1 to 120:1. Concentrated solutions are more expensive, and a higher drag-out* rate is incurred in operation, but they are less sensitive to minor changes in concentration and metallic contaminants are therefore easier to control. The throwing power+ of chromium plating baths is notoriously poor, but the best results are obtained at chromic acid concentrations of 250-300 g/l. Current efficiency in chromium plating is very low compared with most other metals. Efficiency values of more than 12% are not easily obtainable in conventional plating baths. High-efficiency baths, in which anions such as fluoride, fluorosilicate, fluoroborate or other complex fluorides are present enable efficiencies up to 25% to be achieved without using excessively high current densities.

At such low current efficiencies it is obvious that copious amounts of hydrogen must be liberated at the cathode. Hydrogen evolution causes a substantial amount of spray to be formed, and this must be controlled for health and safety reasons. It is normal practice to remove spray by suction and some of the chromium content is lost, but a large proportion can be recovered in simple towers containing Raschig rings or by scrubbing. The more modern plants have installed this type of equipment. Alternatively spray loss can be prevented by use of a surfactant to form a foam blanket. This can only be done for decorative chromium plating because for layers thicker than 25 μm the presence of the foam causes pitting.

The use of electrodeposited chromium coatings in engineering practice depends upon a unique combination of properties i.e. high hardness, good wear resistance, low coefficient of friction, non-stick characteristics and good corrosion resistance. Examples of the applications of hard chromium deposits include inspection tools such as gauges and micrometers, cutting tools, where the anti-stick properties enable the swarf to fall clearly away from the tool, and shafts and valves in pneumatic and hydraulic equipment. Chromium is also used to coat piston rings, cylinder liners for diesel

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[*] drag-out is the term given to the removal of electrolyte when plated objects are withdrawn from the bath.

[+] current density varies from point to point over the electrodes, particularly when complex shapes are being plated. Therefore more or less uneven deposits are obtained depending upon electrode geometry. Many plating solutions have the ability to ameliorate this effect to some degree, and throwing power is a qualitative indication of the extent of this property.

engines, disc brake parts, and undercarriage components for aircraft. The rollers of rolling mills are often chromium plated.

The baths used are very similar in formulation to those used in decorative chromium plating, except that the more concentrated solutions are not often employed, the usual composition range being 150-300 g/l of chromic acid. Higher temperatures and current densities are used than are employed for decorative plating.

Electrodeposited chromium coatings are normally cracked because high tensile stresses are developed in the surface layers. Deposition conditions can be modified to ensure that the chromium layer is uniformly micro-cracked. If such a micro-cracked layer is used in a decorative nickel plus chromium coating, corrosion is spaced out over a large area with a consequent decrease in the anodic current density and the nickel coating is not penetrated rapidly. For engineering applications where there is no nickel layer methods of plating crack-free deposits have been developed. Corrosion resistance is then improved but at the expense of some sacrifice in hardness.

Because of the poor throwing power in hard chromium plating, coatings thicker than about 50 µm have to be finished to size by grinding under controlled conditions. The fatigue strength of components can be impaired by poor grinding techniques, and designers often prefer to specify uniform, 'as-plated' deposits to avoid possible risks created by grinding.

### 3.3.2 Leather Tanning

The process of tanning consists of treating the hide with an agent to chemically stabilise the collagen fibres, thereby increasing resistance to heat, hydrolysis and micro-organisms. Although the oldest form of tanning makes use of the natural tannins, which are polyphenolic plant extracts, most leather is now tanned with solutions of basic chromic sulphate. For example the chrome tanning of cattlehide to produce light leather accounts for some three quarters of the wet-salted cattlehide processed in the UK and is by far the largest domestic tanning activity.

The ability of leather to withstand hot water without curling or shrinking is a valuable criterion of proper chromium tannage. A satisfactory chromium tanned leather must not begin to shrink below 95°C immediately after completion of the tannage. This leather will also be resistant to the action of boiling water after it has been through all of the tannery processes, and the tannage has aged. The minimum chromium requirement for such tannage is 3 grams chromium trioxide per 100 grams of hide substance. Chromium tanning is a very straightforward process in which the conditions are not critical and it is fairly cheap. The only disadvantage is the strong colour of the chromium tanned hide.

The main chemicals used in the industry are basic chromium III sulphate, $Cr(OH)SO_4$ or sodium dichromate which is reduced on site. There are two main tanning methods. The most common is to place the leather in an aqueous solution of basic chromic sulphate. This trivalent-chromium has a rather low average efficiency of chromium uptake and a substantial proportion of the chromium can be wasted in spent tanning liquors. In contrast very high efficiencies are claimed for some chromium VI tanning processes, presumably using sodium dichromate at very low pH in a two-bath tannage. Two bath processes have been abandoned in many countries, to a large extent because of the potential hazards associated with the disposal and possible spillage of hexavalent chromium solutions.

### 3.3.3 Pigments

Pigments are used to impart stability and persistence of colour to surfaces especially in harsh environments. The addition of other useful properties, such as rust inhibition, is also important. Chromium pigments represent the largest outlet for sodium dichromate, the main ones being lead and zinc chromates. A whole range of colours from lemon yellow to orange and red is produced by co-precipitation of lead chromate with lead sulphate and lead molybdate. Green pigments are produced by co-precipitation with copper phthalocyanine or prussian blue. Zinc chromate is used mainly as a corrosion inhibitive primer for metals; lead silico-chromate and strontium chromate are also used for their anti-corrosion properties. Chromium oxide is the basis of a range of green pigments, but in comparatively small quantities.

The outstanding feature of lead chromate pigments is their very high opacity. In addition they are very bright and when surface treated with metal oxides can yield excellent durability. These factors make them ideal for low cost high quality paints and therefore they find their major use in industrial finishes and automotive outlets. Concern about the toxicity of lead has led to a sharp decline in the use of lead chromates in decorative paints, toy, pencil and graphic instrument finishes, and printing inks.

Zinc chromate is by comparison with lead chromates a much more soluble pigment. It is less opaque, duller and of a greenish yellow hue. There has been concern recently about the carcinogenic hazard associated with hexavalent chromium compounds. A recent UK study[3] suggested that this hazard was more likely to be associated with the manufacture of zinc chromate than lead chromate. Following the publication of this report there appears to have been a swing away from zinc chromate towards zinc phosphate and molybdate pigments for use in corrosion protective coatings. Lead chromates are not widely used in primer finishes due to the potential lead toxicity problems when flame cutting and welding.

### 3.3.4 Timber Preservation

Wood can be treated with copper-chromium-arsenic (CCA) compounds as a protection against attack by insects and fungi. These consist of a mixture of copper sulphate, sodium dichromate and arsenic pentoxide in aqueous solution. The chromium acts as a fixing agent, causing the active agents copper and arsenic to remain in the wood in solid form rather than passing out in solution. The nominal compositions of the active ingredients according to the British Standard Specification are given in Table 13.

TABLE 13. - Nominal Composition of CCA Preservatives

| Ingredient | % by weight | |
|---|---|---|
| | Type 1 | Type 2 |
| Copper (as $CuSo_4.5H_2O$) | 32.6 | 35.0 |
| Dichromate (as $Na_2Cr_2O_7.2H_2O$) | 41.0 | 45.0 |
| Arsenic (as $As_2O_5.2H_2O$) | 26.4 | 20.0 |

### 3.3.5 Corrosion Inhibitors

It is standard practice to use corrosion inhibitors to protect metal surfaces in cooling systems in the process industries. Totally enclosed cooling systems are sometimes used, but the most common arrangement is the open evaporative recirculation system employing cooling towers. Chromate salts have been used as corrosion inhibitors for many years and are still the basis of many of the formulations currently used. Older systems used chromate alone for anodic protection, but a high concentration (200-500 g/m$^3$ as $CrO_4$) was necessary, and this is generally considered to be undesirable except in totally enclosed systems. Modern practice is to use a mixture of anodic and cathodic inhibitors. A combination of zinc and chromate, for example, enables a much lower concentration of chromate to be used. A typical formulation would contain 20- 25 g/m$^3$ chromate and 1-5 g/m$^3$ zinc.

### 3.3.6 Other Uses

Chromium compounds are used in the dyeing of textiles, but this use has greatly diminished in the past few years, and less than 1% of dyeing processes now use chromium compounds. Sodium dichromate is used as an oxidising agent in sulphur-based dyeing processes and as a mordant in wool dyeing processes.

Chromium catalysts are used in the synthesis of ammonia and methanol and for many hydrogenation and polymerisation reactions. This is an important application, but the quantities of chromium involved are very small.

Chromium is used in chromium dioxide magnetic tapes, which are manufactured in the Community under licence from Du Pont in the USA. The magnetic tapes are used in audio and video products.

A possible important future use for chromium may be electroplated black chromium coatings for solar collectors.

## 4. CONSUMPTION OF CHROMIUM WITH SPECIAL REFERENCE TO THE EEC

The only major consuming countries to publish consumption statistics on chromite and its derivatives are the United States, Canada and Japan. An analysis of consumption patterns for other countries including the nine member States of the Community must therefore be based upon published trade and production statistics. The importance of the Community as a consumer of chromite may be illustrated by the fact that its consumption has approximately equalled that of the largest individual consumer, the USA, for several years.

World production and consumption of chromite increased at an average rate of approximately 3.8% annually over the period 1950 to 1976, but the rate of increase was much more rapid, exceeding 6%, from 1963 onwards. The proportion of consumption attributable to the centralised economies has declined in the last fifteen years from over 25% to less than 20% of the total. On the other hand, there has been a sharp increase in chromite consumption in South Africa due to the establishment of ferrochromium plant based on indigenous chromite and coal.

In the absence of actual consumption figures, estimates of total apparent consumption of chromium in all forms within the Community are given for the years 1975 to 1979 in Table 14. As there is no mine production within the Community, the "net import" figures for chromite can also be regarded as indicating apparent consumption. The estimates are based entirely upon trade returns for movement of chromium-bearing materials in extra-EEC trade. As an indication of EEC consumption, the totals must be regarded as very approximate. They take no account, for example, of stock build-up or dispersal, and little can be deduced from them except that, in the years 1975 to 1978, annual consumption of chromium in all forms within the Community amounted to about 500,000 tonnes exclusive of secondaries.

Possibly the most significant trend revealed in Table 14 is the steep decline in apparent consumption of chromium contained in ores and concentrates. This is balanced by an increase in the chromium content of ferro-chromium imports, probably reflecting rising demand for "charge chrome" from South Africa, which is successfully expanding its own ferro-chromium capacity to the detriment of European producers.

This overall shift in the make-up of net imports of contained chromium is masked by a rise in total apparent consumption during 1976. Closer analysis, however, reveals that this was due to a sharp increase in imports of ferro-chromium in that year whereas the complementary sharp decline in imports of ore and concentrates appears to have been delayed by two years. The lag can probably be attributed to the gradual expiry of supply contracts for ore and concentrate following a sudden influx of foreign ferrochromium.

## TABLE 14. - Calculation of Apparent Consumption of Chromium in the Community

| | Extra-EEC Imports | Extra-EEC Exports | Net Imports | % Cr | Estimated Chromium content |
|---|---|---|---|---|---|
| | thousand tonnes | | | | thousand tonnes |
| a) 1975 | | | | | |
| Ores and concentrates | 1,271 | (d) 8 | 1,263 | (30) | 379 |
| Oxide and hydroxide | 5 | (a)(d) 6 | -1 | 65 | -1 |
| Chromates | (d) 2 | (d) 3 | -1 | 20 | |
| Dichromates | (d) 8 | (b)(c)(d) 7 | 2 | 30 | |
| Ferro-chromium | (d) 206 | (d) 22 | 184 | 60 | 111 |
| Ferro-silico-chromium | (d) 20 | (d) 0 | 20 | 35 | 7 |
| Metal | (d) 0 | (d) 1 | -1 | 99 | -1 |
| | Total apparent consumption | | | | 495 |
| b) 1976 | | | | | |
| Ores and concentrates | 1,289 | (d) 10 | 1,279 | (30) | 384 |
| Oxide and hydroxide | 3 | (a)(d) 6 | -3 | 65 | -2 |
| Chromates | (d) 3 | (d) 3 | | 20 | |
| Dichromates | (d) 9 | (b)(c)(d) 9 | | 30 | |
| Ferro-chromium | (d) 308 | (d) 35 | 273 | 60 | 164 |
| Ferro-silico-chromium | (d) 27 | (d) 1 | 27 | 35 | 9 |
| Metal | (d) 0 | (d) 2 | -2 | 99 | -2 |
| | Total apparent consumption | | | | 553 |
| c) 1977 | | | | | |
| Ores and concentrates | 1,103 | (d) 7 | 1,096 | (30) | 329 |
| Oxide and hydroxide | 2 | 9 | -6 | 65 | -4 |
| Chromates | (d) 3 | (d) 2 | 1 | 20 | |
| Dichromates | (d)(14) | (b)(c)(d) 7 | 7 | 30 | 2 |
| Ferro-chromium | (d) 299 | (d) 21 | 278 | 60 | 167 |
| Ferro-silico-chromium | (d) 21 | (d) 0 | 21 | 35 | 7 |
| Metal | (d) 1 | (d) 2 | -2 | 99 | -1 |
| | Total apparent consumption | | | | 500 |
| d) 1978 | | | | | |
| Ores and concentrates | (d) 897 | (d) 7 | 890 | (30) | 267 |
| Oxide and hydroxide | 3 | (b) 4 | -1 | 65 | -1 |
| Chromates | (d) 3 | (d) 2 | 1 | 20 | |
| Dichromates | (d)(12) | (b)(c)(d) 8 | 4 | 30 | 1 |
| Ferro-chromium | (d) 388 | (d) 15 | 373 | 60 | 224 |
| Ferro-silico-chromium | (d) 10 | (d) 0 | 10 | 35 | 3 |
| Metal | (d) 1 | (d) 2 | -1 | 99 | -1 |
| | Total apparent consumption | | | | 493 |

Note: Figures in parentheses include some estimated data as full information is not available.

(a) Excludes chromic oxide for the United Kingdom
(b) Excluding Federal Republic of Germany
(c) Excluding United Kingdom
(d) Excluding Irish Republic

Source: IGS compilation

Salient features of chromium consumption patterns in individual European countries are noted in the following paragraphs.

Ferro-chromium is not produced in Belgium and requirements for its stainless steel industry are imported from South Africa, Finland and the USSR. The country has considerable trade, both in exports and imports, in chromium chemicals.

In France the only important consumer of chromite for production of ferro-chromium is Pechiney Ugine Kuhlmann. This combine previously owned mines in the Malagasy Republic which were the source of the chromite consumed. Following nationalisation of these mines PUK will doubtless be turning to alternative supplies. With the interruption in supplies of Madagascan chromite, PUK ceased production of chromium chemicals in 1976 and French requirements were thereafter met by imports from West Germany.

West Germany is the Community's largest producer and consumer of ferro-chromium and in consequence is also the largest importer of chromite obtained mainly from South Africa and the USSR. One West German company, Elektrowerk Weisweiler GmbH, is engaged in ferro-chromium production. South Africa is also a principal supplier of ferro-chromium to West Germany. In addition, South Africa is the country's principal source of chemical-grade chromite which is processed by Bayer A-G, the biggest producer of chromium chemicals in Europe. Chromium metal is produced in West Germany by Gesellschaft für Elektrometallurgie MbH and most of this company's output is consumed domestically. A number of companies are engaged in the production of chromium-based refractories.

Ferro-chromium is produced in Italy on a large scale mainly by Montedison and is also imported, principally from West Germany. A proportion of Italian consumption of chemicals and refractories is manufactured domestically. The sources of chromite consumed by Italy include Turkey, which accounts for about one half, and Albania, South Africa and USSR supplying the remainder.

No chromium-based commodities are produced within the Netherlands and all domestic consumption is derived from imports.

The import of chromite and ferro-chromium into the United Kingdom is almost solely destined for domestic consumption. Unlike West Germany, for example, the United Kingdom does not produce ferro-chromium and is only a modest importer of chromite, consumption of which has been decreasing in recent years. In contrast imports of ferro-chromium have been rapidly increasing and the country is the third largest importer of this commodity in the world with supplies being obtained from South Africa and Sweden. As all chromium for metallurgical purposes is imported into the United Kingdom in the form of ferro-alloy, and, in general, imports of chromite from the Philippines are devoted entirely to the manufacture of refractories, an estimate of the quantities consumed under the categories metallurgical, chemical and refractory can be readily derived.

The consumption of chromium-based commodities in Ireland and Denmark is assumed to be met fully by the import of such commodities in manufactured form from elsewhere.

## 4.1 Consumption of Chromium by End-Use

The compilation of end-use consumption statistics for chromium is difficult because data for most countries are sparse and often not directly comparable. The most complete statistics are available for the USA, in a very comprehensive study of chromium consumption, uses, and the potential for conservation[4]. Table 15 summarises the estimated consumption pattern for the USA in 1977. Statistics and projections to 1985 for world consumption of chromite were presented in a less detailed form in a 1975 German study[5] (Table 16). As far as the Community is concerned this study indicated that approximately two-thirds of consumption were in metallurgical applications and this proportion was gradually increasing. Chemical uses were remaining steady at about 22%, and there was a gradual decline in consumption in refractories.

TABLE 15. - USA Chromium Consumption Patterns 1977

| End-use | % USA Consumption |
|---|---|
| Metallurgical | |
| Wrought stainless and heat-resisting steels | 51.3 |
| Tool steels | 1.3 |
| Wrought alloy steels | 9.5 |
| Cast alloy steels | 3.1 |
| Alloy cast irons | 1.8 |
| Non-ferrous alloys | 3.1 |
| Other | 1.3 |
| Sub total | 71.4 |
| Refractories | |
| Chrome and chrome-magnesite | 2.2 |
| Magnesite-chrome brick | 3.1 |
| Granular chrome-bearing | 6.0 |
| Granular chromite | 2.2 |
| Sub total | 13.5 |
| Chemicals | |
| Pigments | 4.0 |
| Metal finishing | 3.3 |
| Leather tanning | 2.4 |
| Drilling muds | 0.7 |
| Wood treatment | 0.9 |
| Water treatment | 0.9 |
| Chemical manufacture | 1.1 |
| Textiles | 0.4 |
| Catalysts | <0.3 |
| Other | 1.1 |
| Sub total | 15.1 |
| Total | 100.0 |

Source: Reference 4

TABLE 16. - World Chromite Consumption by Sector

| | % of Chromite Consumption | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Metallurgical* | | | Chemical | | | Refractory | | |
| | 1973 | 1980 | 1985 | 1973 | 1980 | 1985 | 1973 | 1980 | 1985 |
| EEC total | 62.5 | 64.1 | 67.1 | 22.5 | 22.6 | 22.4 | 15.0 | 12.8 | 10.5 |
| USA total | 65.7 | 68.5 | 72.9 | 15.2 | 16.2 | 15.4 | 19.1 | 15.3 | 11.7 |
| Western bloc total | 76.2 | 78.2 | 80.3 | 11.3 | 11.1 | 10.6 | 12.5 | 10.7 | 9.1 |
| Eastern bloc total | 64.0 | 68.0 | 72.0 | 14.7 | 11.5 | 8.4 | 21.3 | 20.5 | 19.6 |
| World total | 73.8 | 76.2 | 78.7 | 12.0 | 11.2 | 10.2 | 14.2 | 12.6 | 11.1 |

Source: Reference 5

* It is not clear from the German study whether chromium metal for superalloys is included here. Because it is manufactured from chromic oxide it is probably included in the chemical sector.

There appears to be considerable variation between the consumption patterns for the various member countries. This is illustrated in Table 17, which has been compiled from data supplied during the present study. Most of the variation is between refractory and chemical uses, however, and consumption in metallurgical applications is dominant in all countries. Also there may be variations in the way the statistics are calculated.

TABLE 17. - Distribution of Chromium Consumption in Community Countries

| End-Use Sector | % of total consumption | | | | |
|---|---|---|---|---|---|
| | Denmark 1977 | France 1976 | Germany 1977 | Italy 1978 | UK* 1975-8 |
| Metallurgical (steels only) | 68 | 84 | 70 | 80 | 50 |
| Refractory | 20 | 7 | 4 | 2 | 20 |
| Chemical (includes Cr metals) | 12 | 9 | 26 | 18 | 30 |

* These data refer to consumption by the three primary industries. They do not take into account exports of products in the refractory and chemical sectors.

If it is assumed that 65% of chromium consumption in the EEC goes into metallurgical applications, this amounts to about 325,000 tonnes/year. Table 18 shows how this quantity is distributed between different steels, based on the forecasts of the 1974 ECSC Special Steels Working Party[6], and 1977 estimates for Germany and the UK. There is no up-to-date information on the distribution within the Community as a whole, but it seems reasonable to assume the 1974 forecast was accurate.

TABLE 18. - Distribution of Chromium Consumption in Steels, %

| | ECSC 1980 forecast | UK 1977 | Germany 1977 |
|---|---|---|---|
| Stainless Steels | 80 | 69 | 90 |
| Engineering Steels | 16 | 29 | 10 |
| Tool and High Speed Steels | 4 | 2 | |

Chromium consumption in refractories is about 64,000 tonnes/year. There has been a marked decline in the use of chromite in all sectors. This is illustrated here by reference to UK production and consumption statistics, but the trends are similar in other countries. Because the steel industry is the main consumer of chromite-bearing refractories trends in that industry have a dominant influence on the consumption of chromite. This is shown in Fig. 7, which also includes projected trends for 1980 and 1985. Basic brick production, with a forecast up to 1990 by a major UK producer, is summarised in Fig. 8. The very steep drop in the production of chromite-magnesite bricks reflects the closure of open-hearth furnaces since 1970. Other factors which are reducing consumption are discussed in Chapters 3 and 5.

Chromium consumption in chemicals amounts to about 113,000 tonnes/year. Table 19 shows the estimated distribution of this chromium averaged out from data on consumption in France, Germany, Italy and the UK. There are very considerable variations between

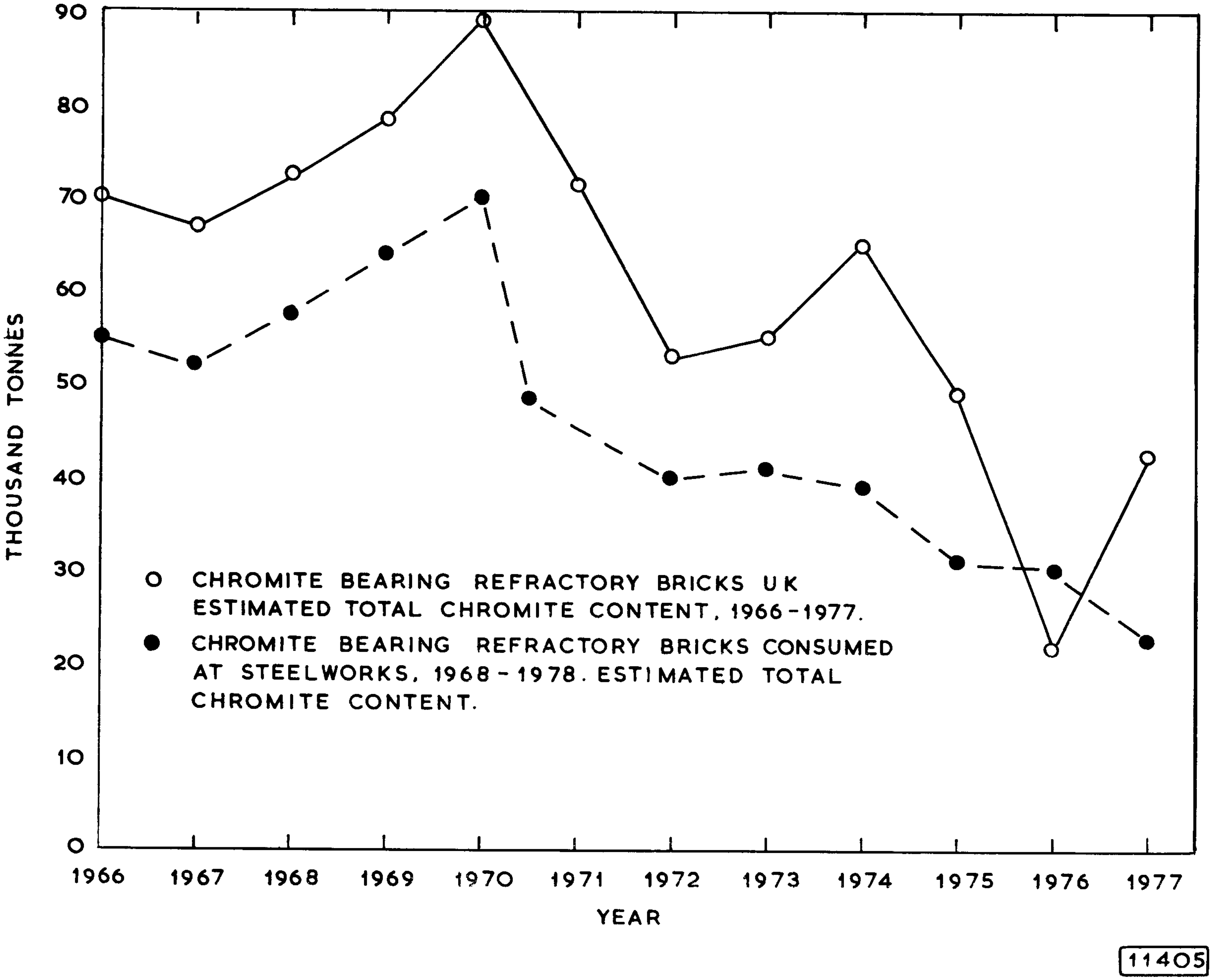

FIG.7 CHROMITE CONTENT OF REFRACTORY BRICKS

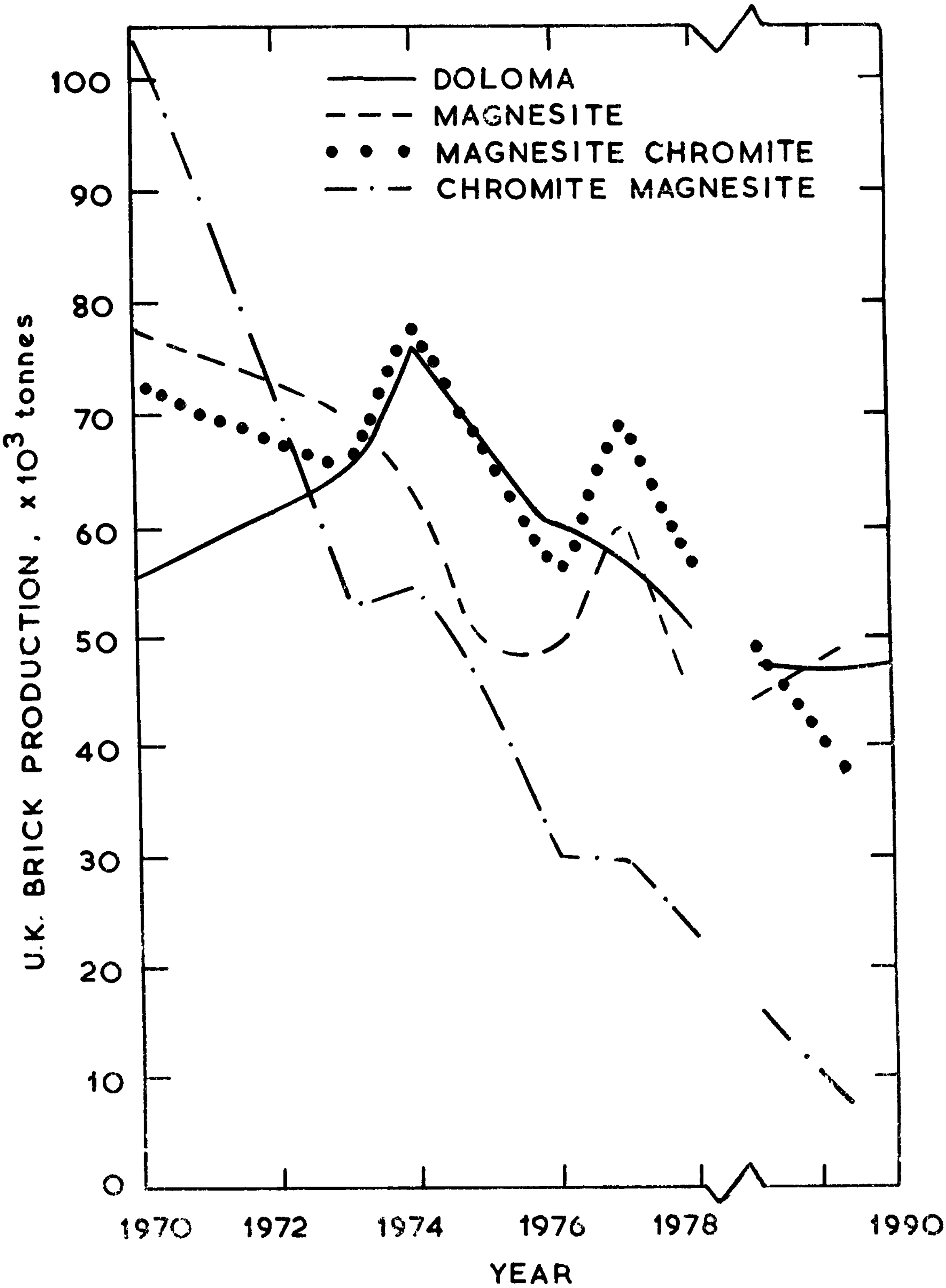

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FIG. 8 SUMMARY OF ACTUAL AND FORECAST U.K. PRODUCTION OF SHAPED BASIC BRICK PRODUCTS countries, but comparisons are difficult because of the different ways in which statistics are classified.

TABLE 19. - Distribution of Chromium Consumption in Chemicals

(Average for France, Germany, Italy, UK)

| | % |
|---|---|
| Chromium Sulphate (mainly tanning) | 34 |
| Chromic Acid (electroplating) | 15 |
| Chromates (mainly wood preservation, pigments (but other miscellaneous uses included) | 23 |
| Chromic Oxide (Cr metal, pigments, ceramics) | 28 |
| | 100 |

By far the greatest proportion of chromium goes into alloy steels, but it is unfortunately very difficult to obtain data on the market distribution of the steel products. The data that are available are not directly comparable, and therefore they are quoted separately in Tables 20-22.

TABLE 20. - Western Europe and USA: Stainless Steel End-Uses in 1971

| Sector | Western Europe, % | USA, % |
|---|---|---|
| Chemical and food processing | 39 | 16 |
| Consumer durables | 38 | 18 |
| Transport | 7 | 26 |
| Building and construction | 3 | 6 |
| Others | 13 | 34 |
| | 100 | 100 |

Source: Economics of Chromium 3rd Edition, Roskill Information Services 1978

TABLE 21. - Expected UK Consumption of Stainless Steel Flat Products 1981-82

| Sector | % |
|---|---|
| Process and Power | 31 |
| Building | 15 |
| Transport | 18 |
| Consumer Goods | 19 |
| Commercial Catering | 9 |
| Others | 8 |
| | 100 |

Total Production ca 110,000 tonnes (tentative figure)
Flat Products ca 65% of stainless steel production
Source: British Steel Corporation

TABLE 22. - Steel Alloy Consumption in Germany, 1977

| Sector | % |
|---|---|
| Mechanical engineering | 30 |
| Manufacture of finished products and tools | 19 |
| Vehicles | 16 |
| Pipes and forgings | 11 |
| Electrical engineering | 7 |
| Construction and Civil Engineering | 6 |
| Others | 11 |
| | 100 |

Source: DIW/ite

Based on the foregoing data, the best estimate of the end-use distribution of chromium consumption in the Community is shown in Table 23.

TABLE 23. - EEC Chromium Consumption Pattern

| End-Use | Consumption | |
|---|---|---|
| | '000 tonnes | % of total Cr |
| Metallurgical | | |
| Stainless Steels | 260 | 52 |
| Engineering Steels | 50 | 10 |
| Tool Steels | 15 | 3 |
| Refractory | | |
| Refractory Bricks | 50 | 10 |
| Foundry Sands | 15 | 3 |
| Chemical | | |
| Chromium Oxide (for metal production, ceramics, pigments) | 30 | 6 |
| Leather Tanning | 40 | 8 |
| Electroplating | 15 | 3 |
| Wood Preservation, Pigments, Miscellaneous | 25 | 5 |
| Totals | 500 | 100 |

## 5. CHROMIUM SUBSTITUTION AND CONSERVATION

### 5.1 Materials Substitution

Before discussing possible alternatives for chromium in its various applications it is useful to consider substitution and how it occurs more generally. Materials substitution is a widely recognised phenomenon, but the conditions necessary for its occurrence are varied and not always predictable. In its simplest form substitution consists of the use of alternative materials with superior characteristics or lower cost, but the process is often very much more complex than this would suggest. The choice of a material depends on many factors: technical (mechanical and physical properties at operating temperatures, reliability, ease of fabrication, joining etc); economic (costs of raw material, capital equipment, maintenance etc); and many other less easily quantifiable ones, including availability, continuity of supply, consumer preference, environmental effects, and skills of available manpower. In a free market the basic driving force for substitution is cost effectiveness, and this must involve some compromise between these factors.

The competition between copper and aluminium illustrates these points very well. Aluminium has good thermal and electrical conductivity, although not so good as copper, and it is the cheaper of the two metals. On the other hand copper is much easier to join to other metals than is aluminium. The result of the interplay of these factors is that aluminium has been able to make some inroads into the electrical conductor market, particularly in heavy current-carrying cables. It has been much less successful in competing with copper in car radiators because difficulties in joining lead to higher manufacturing costs. Changing from an established material to a new one is a costly process, through the need to modify machinery and purchase new equipment. The price differential between competing materials must be sufficiently large for the change to be worthwhile. In 1974 when the price differential between copper and aluminium was £1000/ tonne there were great attractions in using aluminium in electrical conductors despite copper's greater technical appeal. Only a year later the differential was only £200/ tonne and the incentive had largely disappeared.

Generally speaking successful substitution depends upon the entrepreneurial spirit of the manufacturers of new materials who want to expand their markets. Indeed, in many cases it is not so much a matter of a new material replacing an established one, but rather an expansion into new fields which could not previously be satisfactorily exploited, as is suggested, for example, by the remarkable growth in the use of plastics in packaging. It is, perhaps, more difficult to set out to find an alternative for a specific material. Most new materials substitute for an older one only in a fraction of its applications. Therefore substitution is generally more cautious and slower, the more sophisticated the service, and lead times are long.

A number of important points emerge from this discussion. Due to the increasing complexity of technology it is virtually impossible for a new material to be superior to an established one in all respects. There is intense competition between materials and large sums are spent on promoting market penetration of new materials. This stimulates the producers of more traditional materials to defend their markets and make their product more cost effective. The end result is frequently that the consumer benefits from a better or cheaper product even if the substitution is not successful. This is well illustrated by developments in the beverage can industry, where tin-plate continues to withstand vigorous competition from aluminium and tin-free steel. It is important to note that much of the R and D was undertaken as a consequence of commercial activities, and was not the cause of them.

In the case of chromium the motivation for substitution is not the usual one of having developed a new material with interesting properties for which an outlet is sought. Instead it arises from a concern that an essential constituent of materials which are critically important to industry might be subject to interruptions in supply. Whether or not this relatively unfamiliar driving force for substitution should be limited by the same economic constraints as purely commercial activities is essentially a political judgement, but there is no doubt that it poses additional problems. Chromium has been historically a relatively low-cost and plentiful material which confers unique properties on a wide variety of alloys and compounds. Previous research efforts have been devoted more to seeking improvements in properties by increasing chromium contents than to searching for chromium-free substitutes. This is particularly true of the largest area of application in stainless steels and other alloys; there has been some interest in replacing chromium in some chemical applications, but stimulated by pollution control problems rather than concern about raw material supplies.

In the remainder of this chapter substitution for chromium in its end-uses will be considered in detail. It will be seen that in some applications, notably refractories, substitution has already taken place to some extent for economic reasons and the trend may be expected to continue. In other applications more or less adequate substitutes are available, but at considerably higher cost, and there will be little desire from industry to use alternative materials unless they are compelled to do so. In the case of alloys, complete replacement of chromium is generally not possible without unacceptable loss of performance, but there might be opportunities to reduce the amount required to meet a desired specification. Another possibility is to use new processes which are less wasteful, or confer longer life on a chromium-containing product. Finally there is scope to conserve appreciable quantities of chromium, and at the same time to reduce adverse effects on the environment, by recycling.

## 5.2 Recycling

Opportunities for increasing the extend of chromium recycling occur mainly in its chemical applications. Although these individually only account for a small proportion of consumption, wastage rates are high and there is concern about the impact of chromium-bearing wastes on the environment, particularly in the highly toxic hexavalent state. Recycling is practiced to some extent in the electroplating industry, and the overall efficiency of chromium usage could be as high as 95%, but this is rarely achieved. In practice it is probably between 25 and 50%, but it is difficult to get reliable statistics because of the wide variations between the activities of different companies. Similarly high efficiencies of 95% or more are feasible in the tanning industry, but the average is 70-75%. Community losses of chromium in the electroplating and tanning industries alone could therefore be of the order of 20,000 tonnes/year.

## 5.3 Stainless Steels

About 80% of metallurgical chromium consumption (50% of the total) goes into stainless steels. The other metallurgical applications are individually both much smaller and more difficult to substitute. Stainless steels are therefore considered in greater detail than the other metallurgical applications. The information is based upon discussion with co-pilots, industrial organisations and one of the authors' (GL) research experience, supplemented by reference to the American National Research Council study of chromium substitution[4], and the excellent surveys of alloying clements commissioned by DGIII[6,7].

As described in Chapter 3 it has long been accepted that something in the region of 12-13% chromium is necessary to give reliable resistance to either wet corrosion or high temperature oxidation, and that further increases in chromium content produced more resistant materials. This factor has, however, to be balanced against other considerations, such as the need to stabilise the austenitic structure, mechanical strength, brittleness, hardenability, stress-corrosion cracking, deep-drawing properties and structural stability. In the field of high-temperature materials it was found over many years that alloys containing sufficient chromium to confer adequate high temperature mechanical strength possessed more than adequate resistance to oxidation at the temperatures at which their mechanical properties made them useful. More recently, however, alloys have been formulated to maximise mechanical strength at high temperature which contain insufficient chromium to resist oxidation and corrosion, so that either these materials must be protected by coatings or a compromise must be reached between strength and chemical resistance to an environment. Similarly, with stainless steels of the austenitic type, the basic 18% Cr/8% Ni formulation has been upgraded to contain up to 20-30% of each element, with additions of aluminium, silicon, molybdenum etc. for resistance to highly corrosive liquids and oxidising, carburising and sulphiding gases. These developments have been limited by the need to maintain acceptable mechanical properties and weldability, and the corrosion resistance of welds has been safeguarded by controlling the carbon content and including adequate proportions of stabilising elements.

In a crisis, if it lasted long enough to make a serious substitution programme necessary and could not be countered by drawing on stocks, it seems probable that the main saving would be made in the mass of trivial applications which could be substituted by chromium-free materials. There would be penalties in loss of convenience and attractiveness of products, and associated costs for new and modified production equipment. An attempt to distinguish between those applications where stainless steel is indispensible and those where substitution would be relatively straightforward is made in the Italian report (Appendix A, p.12). No doubt such a classification would be disputed by the various consumer industries, who would regard substitution as unacceptable under normal market conditions. Nevertheless it is reasonable to suggest that stainless steel is not essential in many of its uses in furniture, architecture, domestic equipment and the food production industry. The grades of steel used in these industries are 11-13% chromium ferritic and martensitic steels (type 409 and 410), type 304 austenitic and some higher grade materials such as type 316. Necessary properties are resistance to atmospheric corrosion and to corrosion by mildly aggressive solutions. Because of its ready formability type 304 is frequently used where ferritic stainless steel of lower chromium content would give adequate corrosion resistance. Frequently prestige, ease of cleaning, appearance or vandal-proofing are important in selection of materials, and a high proportion of the stainless steel used could be eliminated by substituting painted or vitreous-enamelled mild steel, other metallic coatings or aluminium.

Stainless steel could be eliminated almost entirely from many of its uses in the transport sector, and a trend in this direction is under way, but emission control equipment for cars represents a new and quite important application for chromium-containing alloys[8]. Any future legislation on exhaust emissions might be waived in an emergency, but new developments would be needed to reduce chromium contents below 15-25%. Also stainless steels with 12-18% chromium are increasingly being used for conventional exhaust systems where they are resistant to low-temperature condensate corrosion as well as high temperature oxidation. Aluminised mild steel could be used, but some modification in mechanical design would be needed.

Much more difficult problems would arise in the chemical engineering, power generation and nuclear industries. Stainless steels are used for a variety of reasons, including the high-temperature strength due to the austenitic structure, and resistance to corrosive solutions and high temperature oxidation. A wide range of operating conditions is involved, including strong acids and alkalis, contamination by molten salts, and oxidising, carburising and sulphiding environments. At present high chromium contents (18-25%) are quite indispensable for many of these applications, and there would be strong and perfectly reasonable reservations about any suggestion for using substitute materials without convincing long-term operating experience. Coatings might offer a possible solution in some cases, but they would make corrosion more damaging once they were mechanically breached, and so vitreous enamel or thin metallic coatings would be unsuitable for many applications. Thick coatings of existing high-chromium alloys on a chromium-free backing might serve (e.g. co-extruded tubes are already in use), or other materials, such as titanium or tantalum, at present excluded by cost or availability, might be used as claddings.

Previous work on the formulation of stainless steels has not for the most part represented an attempt to substitute for chromium, because chromium has been historically a relatively cheap and abundant material. A previous EEC report[6] on substitution of alloying elements in special steels concluded that the main purpose of research in this field was to save nickel, and that there was no alternative to chromium in stainless steels. The report forecast that production of series 300 steels would gradually decline because of two probable trends:

1) The introduction of Cr-Mn-Ni-N (Nitronic) grades with which, by virtue of their excellent mechanical characteristics over a wide temperature range, up to 50% of the weight of steel can be saved without forfeiting resistance to the various types of corrosion in engineering applications where thickness is needed for mechanical strength.

2) The development of ferritic steels with low interstitial element content, which, being more resistant to stress corrosion and (if stabilised with titanium or niobium) intergranular corrosion, will be able to compete with austenitic steels for about half of the market of the latter i.e. mainly chemical applications from room temperature up to 300°C.

It was considered that these trends were likely to permit a reduction in the consumption of nickel in stainless steels both by reducing nickel contents and by reductions in the weight of manufactured products. This would, however, be offset to some extent by an increase in the chromium content required to offset the deleterious effect of eliminating nickel on the corrosion resistance.

While it is certainly true that the presence of chromium in stainless steels is essential, there are indications that some reduction in chromium content might be possible without unacceptable loss in properties. Successful research in this direction depends on achieving improvements in passivity (for wet corrosion) and protective oxide films (for high temperature oxidation). Two such developments are the attempts to reduce chromium contents by adding aluminium or silicon, and to improve aluminium-containing steels with rare-earth additions.

Steels containing chromium with additions of silicon or aluminium for improved resistance have been used for many years: a 6-7% chromium, 1% silicon steel was used for aircraft engine valves during the first world war. Systematic scientific investigations were made comparatively early[9]. Additions of rare earth elements were found to be beneficial, particularly in alloys for electrical resistance heaters[10] and there has been considerable renewal of interest in this possibility in recent years, particularly using yttrium and hafnium[11]. The effects are complex, and probably involve preservation of a fine-grained structure, as well as accelerated nucleation of protective oxide phases, and improved adherence of the oxide. In developing alloys for extremely high temperatures, the beneficial effects of chromium begin to be lost by volatilisation of the higher oxide $CrO_3$, and it is desirable to promote formation of the less volatile $Al_2O_3$ without unduly increasing the aluminium content of the alloy, which would have a deleterious effect on mechanical properties. The role of silicon and rare earth elements in this connection is not well understood, but ferritic stainless steels have been developed suitable for electrical heater elements and some engineering applications, e.g., catalytic convertors for controlling the hydrocarbon content of combustion gases[8]. These materials are of fairly low mechanical strength, and may embrittle after service at high temperature, although additions of yttrium appear to be beneficial from this point of view.

In the USA the NASA Lewis Research Centre in Cleveland has carried out a study of adding aluminium, silicon, molybdenum and manganese to type 304 stainless steel with the intention of obtaining similar properties with reduced chromium contents[12]. The composition of the alloys studied are shown in Table 24.

TABLE 24. - Composition of Modified 304 Stainless Steel Alloys

| | Nominal Chemical Composition, wt. % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mn | Si | Al | Mo | C | Fe |
| 304 Stainless Steel | 18 | 8 | 1.1 | 0.65 | - | - | 0.06 | Bal. |
| 12% Cr-Si (Ferritic) | 12 | 8 | 1.1 | 2.65 | - | - | 0.06 | Bal. |
| 12% Cr-Al-Mo (Ferritic) | 12 | 8 | 1.1 | 0.65 | 2 | 2 | 0.06 | Bal. |
| 12% Cr-Si (Austenitic) | 12 | 10 | 1.1 | 3.65 | - | - | 0.06 | Bal. |
| 12% Cr-Al-Mo (Austenitic) | 12 | 10 | 5.1 | 1.65 | 2 | 2 | 0.06 | Bal. |

The conclusions of this work were that the ferritic alloys could not be considered adequate substitutes for type 304, but that the austenitic alloys showed promise of permitting substantial savings in chromium. Considerable development work, and a better understanding of the mechanisms leading to corrosion and oxidation resistance, would be needed before these new alloys could compete with conventional stainless steels. There is considerable interest in this topic in several member countries, and a belief that useful new alloys could be developed within ten years but probably not less than five years. It should be pointed out, however, that representatives of the stainless steel industry in one member country were very sceptical and stated that they had not been able to reproduce the American results.

A successful development in this area would not reduce chromium consumption by more than one-third, even within the sector of the market it succeeded in penetrating. Larger reductions would require improved understanding of the factors underlying the requirement for a certain chromium content in order to produce either a passive film or a scale which acts as a barrier to the diffusion required for further reaction. Theory and experiment indicate that these limits are based, not on any requirement imposed by the thermodynamic stability of product phases, but on the kinetics of diffusion processes, which can be modified. It is by no means unknown for materials containing less than 12% chromium to show anomalously high resistance to both corrosion and oxidation. It is therefore possible to look at protection from a rather different angle, and instead of assuming that good protection can only be obtained from $Cr_2O_3$ films, and that these will be formed only if chromium contents are greater than 12-13% (neither of which is true), to accept that films of other products can be protective, and to concentrate on understanding and controlling the failure of these films. This approach appears to be valid for both oxidation and wet corrosion, and in both cases the protective film may maintain its structure over most of the surface even during breakdown, rapid reaction being confined to a few isolated starting centres. It has probably been pursued more successfully for high-temperature oxidation than for wet corrosion.

Means have already been developed for modifying the structure of oxide films by trace alloying additions, sometimes combined with preliminary heat treatment, mechanical pre-treatment or surface coatings. The net effect of this type of treatment can often be to confer on an alloy of given chromium content the resistance to oxidation normally obtained with about twice the chromium content. At present these treatments have serious limitations: they are not effective above temperatures of 1000-1100°C, and they may exacerbate trouble due to evaporation of alloying constituents. Also, they do not work well with austenitic stainless steels. More basic research is needed in this general area of the protectiveness and failure mechanisms of oxide films, and the way in which the structure and properties of the film are modified by additions of silicon, aluminium, rare earths, mechanical working and surface treatments with glass-forming materials such as borates, silicates and phosphates.

Similarly there is no good understanding of the nature of passive films in wet corrosion. It is known that chromium plays an important part in stabilising the film, but high chromium content is not the only requirement. The study of passivity by purely electrochemical techniques appears to have become unproductive, but with modern techniques for the study of the composition and microstructure of passive films it should be possible to gain a better understanding of the factors determining resistance to corrosion.

A final, and very important point needs to be made concerning the development of alternatives to currently available stainless steels. This relates to the problems of performance testing. Any attempt to encourage substitution must face perfectly understandable scepticism based on doubts about extrapolating the results of laboratory tests to service conditions. This applies both to newly developed alloys and to coatings and linings. It is not always possible to anticipate all the factors which may influence performance, some of which may not be adequately simulated in tests. Such factors as the designs of joints, welds, deposition of sludge, alternating temperature and stress, and minor impurities in the corrosive environment, may strongly affect corrosion processes. Therefore any attempt to accelerate tests by using elevated temperatures or environments of exaggerated severity may lead to unexpected complications. Also, it is not always clear which kinetic relationship should be used in extrapolating the results of short-term tests. The subject of corrosion testing is confused and uncertain and systematic investigation is needed of the effects of various test parameters on measured rates of corrosion. Community concerted action is already taking place in this field in the technically difficult, but, from the point of view of chromium consumption, less significant area of gas turbine materials (COST 50).

### 5.4 Engineering Steels

The influence of the various alloying elements on mechanical strength over a wide range of temperatures, and their effects on heat treatability have been extensively investigated and are now well understood. For this reason, many possibilities exist for substituting chromium by other carbide-forming elements such as molybdenum, tungsten, vanadium, manganese etc. without sacrificing performance. Addition of chromium is, however, among the cheapest methods of securing the required mechanical performance, and substitution, though frequently quite practicable, will usually lead to a substantial increase in cost at current metal prices. Computer programmes are available for selecting the minimum-cost composition for a particular specificaton at a given set of prices[4]. The optimisation would, of course, lead to different compositions if the price of chromium were to change substantially, but the programmes could presumably be modified to minimise chromium content irrespective of price.

There has been a general movement in recent years by large consumers of alloy steels (e.g. the automotive industry) towards leaner, more cost effective alloys. Because of the high level of investment in production lines, any changes in production techniques required because of a change in steel composition would be difficult and expensive. This is another factor which would cause user resistance to substitution.

Considerable savings in chromium are clearly feasible in this field using existing knowledge, but there would be a substantial cost penalty. The American survey suggested that about 10% of the chromium used in this sector could be eliminated in the short term, and a further 60-70% over a 10 year period. Substitution would be difficult in the area of turbine steels and high temperature materials.

## 5.5 Tool Steels

Tool steels probably account altogether for less than 3% of total consumption of chromium. About 40% of this is for high-speed steels, and most of this, and also the rather smaller demand for cold-work tool steels, could probably be eliminated by using sintered cobalt carbide materials which contain no chromium. The main area where substitution does not seem to be practicable is in hot-work tools, which account for about 20% of the chromium used in this group. Sintered carbides may not be suitable in all cases, and they would certainly be much more expensive than high-speed steels. These materials are vital to the engineering industry, but because they account for such a small share of the market there would be little incentive to minimise chromium consumption. If substitution did become necessary the supply position of some of the alternative materials involved, such as cobalt, would have to be taken into consideration.

## 5.6 High Performance Alloys

Because of their military importance, these materials have been energetically developed, and few promising lines remain unexplored. There is some incentive to reduce chromium content because this increases strength at the highest temperatures, and coatings already developed make it possible to use materials which otherwise would have inadequate resistance to hot corrosion. These coatings consist largely of aluminium and titanium compounds. They often have limited lives, which may be shorter than the creep lives of the basic blade materials, and they can be extremely brittle. Ceramic coatings carry an even greater risk of exposing inherently unsatisfactory material if the coating fails, but some development is proceeding, as also with blades or entire rotors consisting entirely of ceramic materials. The use of coatings is not yet considered adequate to reduce chromium consumption because of the risk of coating failure, and the use of ceramics is unlikely to occur in aero-engines for many years. Progress in this field will probably continue to be slow, and there is little prospect of substantial savings of chromium in the short term. The problem of lead-times for introducing new materials is also particularly difficult, because data from accelerated tests or tests in simulated operating conditions carry little conviction. As mentioned earlier EEC concerted action already exists in this field (COST 50).

The remaining materials comprise a number of rather exotic alloys used in chemical and nuclear plant, electric resistance heaters etc. Chromium is again indispensable in the great majority of cases, and substitution is difficult except where there is scope for clad materials. Carbide resistance heaters can be substituted for nickel-chromium in some cases. There is a certain tendency to over-specify, and aluminium-containing ferritic stainless steels may make it possible to reduce chromium contents for less onerous service conditions.

## 5.7 Refractories

### 5.7.1 Refractory Bricks

In Chapter 4, it was seen that consumption of chromite in refractories is declining, partly due to the obsolescence of the open-hearth furnace, but also because of trends towards the replacement of chromite by other materials. For example, in the electric arc furnace increased use of high purity magnesite and conversion to water-cooled panels in hard driven furnaces are both reducing the demand for magnesite-chromite. The opposing trend towards the use of magnesite-chromite in arc furnace roofs may also be reversed by conversion to water-cooling in the largest furnaces, particularly if there is an increase in the demand for steel. It is clear, therefore, that adequate alternatives to chromite are available for use in the arc furnace. There is a movement towards dolomite in the AOD process, but magnesite- chromite is still preferred in some secondary steelmaking ladles where the slags are silicious. In a few cases non-availability of chromite could be a problem, but tonnages are small, and the problem could be overcome by the development of synthetic magnesium aluminate spinels.

Replacement of magnesite-chromite would present the greatest difficulties in non-ferrous metal refining. In the event of a chromite shortage, the most promising alternative would be a synthetic magnesium alumino-silicate spinel. The necessary development work could be carried out easily within the industry, and indeed the British Ceramic Research Association are already doing some work in this field. The export market for refractories in the non-ferrous metals industry is very important.

### 5.7.2 Foundry Sands

There are three refractory sands which are used in steel foundries. One of these, olivine, is generally regarded as being less satisfactory than the other two. Olivine is a basic material, and for this reason it is widely used for the production of austenitic manganese steel castings. In the Community, the USA and Japan olivine sand is mainly employed for this purpose, but in Scandinavia it is used for producing all types of steel castings as well as iron castings.

The other two refractory sands, chromite and zircon, are much closer together in properties. Indeed, they provide a classical example of how substitution takes place in industry because of primarily economic forces. Zircon sands were introduced in the 1950's and they substantially improved the quality of steel castings. Zircon sands are fine-grained, highly refractory, and offer good resistance to metal penetration. A particularly important characteristic of zircon sands is the consistency in purity and foundry behaviour. This is their main advantage over chromite and many foundrymen were reluctant to change from zircon when chromite sands were introduced, in spite of the fact that chromite was cheaper and gave improved resistance to metal penetration. In the UK chromite gained wide acceptance during 1968 and 1969 but it was not until 1973, when the price of zircon increased dramatically, that many foundries which had resisted changing to chromite finally did so because of economic necessity.

Zircon has suffered from price instability due to the fact that it is a co-product of rutile, and production was relatively small. The very steep price rise in 1973/74 was due to an increasing world demand without a corresponding increase in production. More recently increased production capacity in Australia and user resistance to high prices combined to produce a supply surplus, and during 1978 there was some growth in the foundry market because it was again competitive with chromite. Changes in relative prices and consumption of the refractory foundry sands in the UK are illustrated in Figures 9 and 10.

In summary, this does not appear to be a priority area for R and D. A satisfactory substitute for chromite exists which is much less vulnerable to political pressures.

### 5.7.3 Recycling of Refractories

Destructive consumption of refractory brick in steelmaking is increasing because of the use of the electric arc furnace and the AOD process. Nevertheless, when a

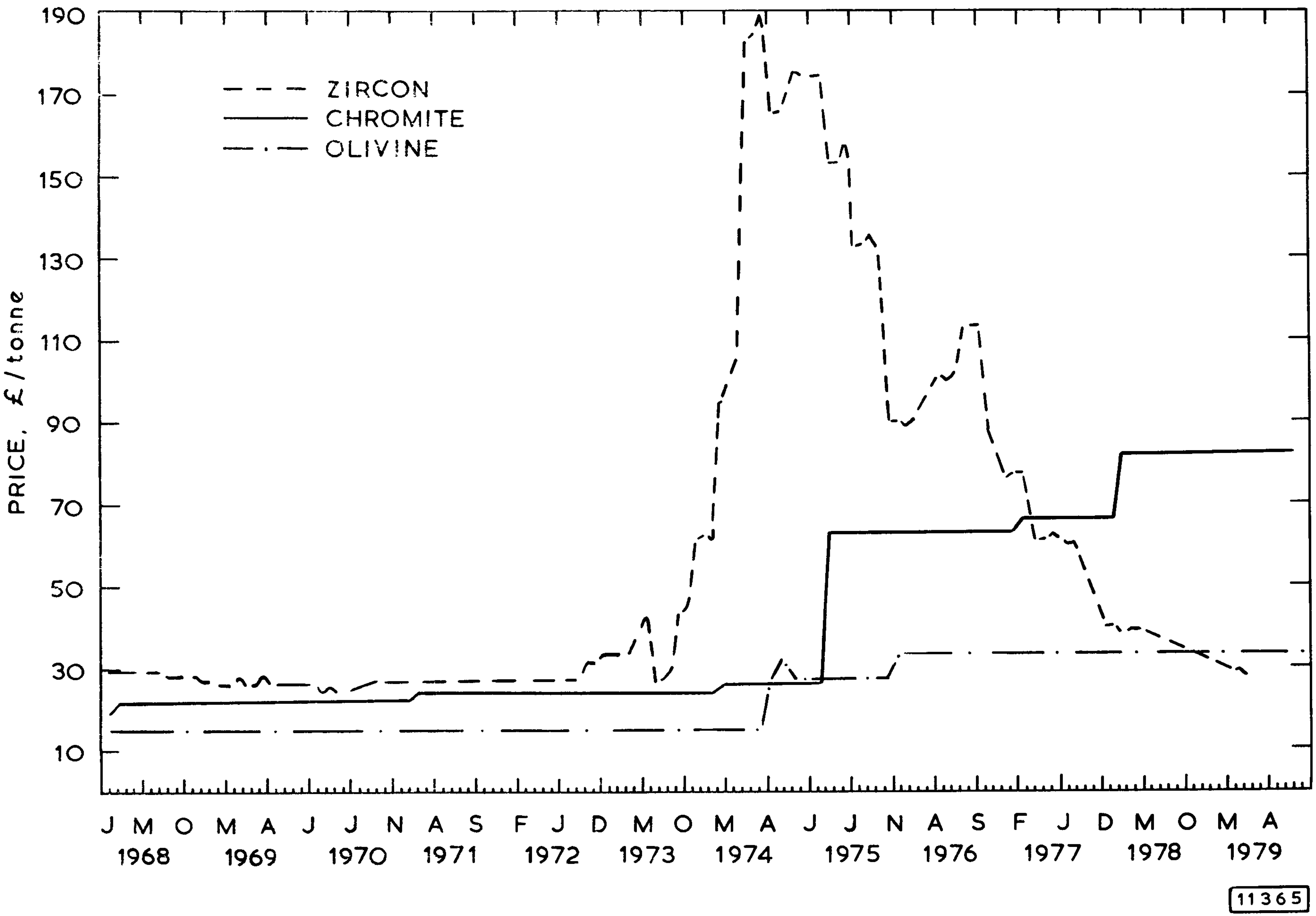

FIG. 9 REFRACTORY SAND PRICES IN U.K.

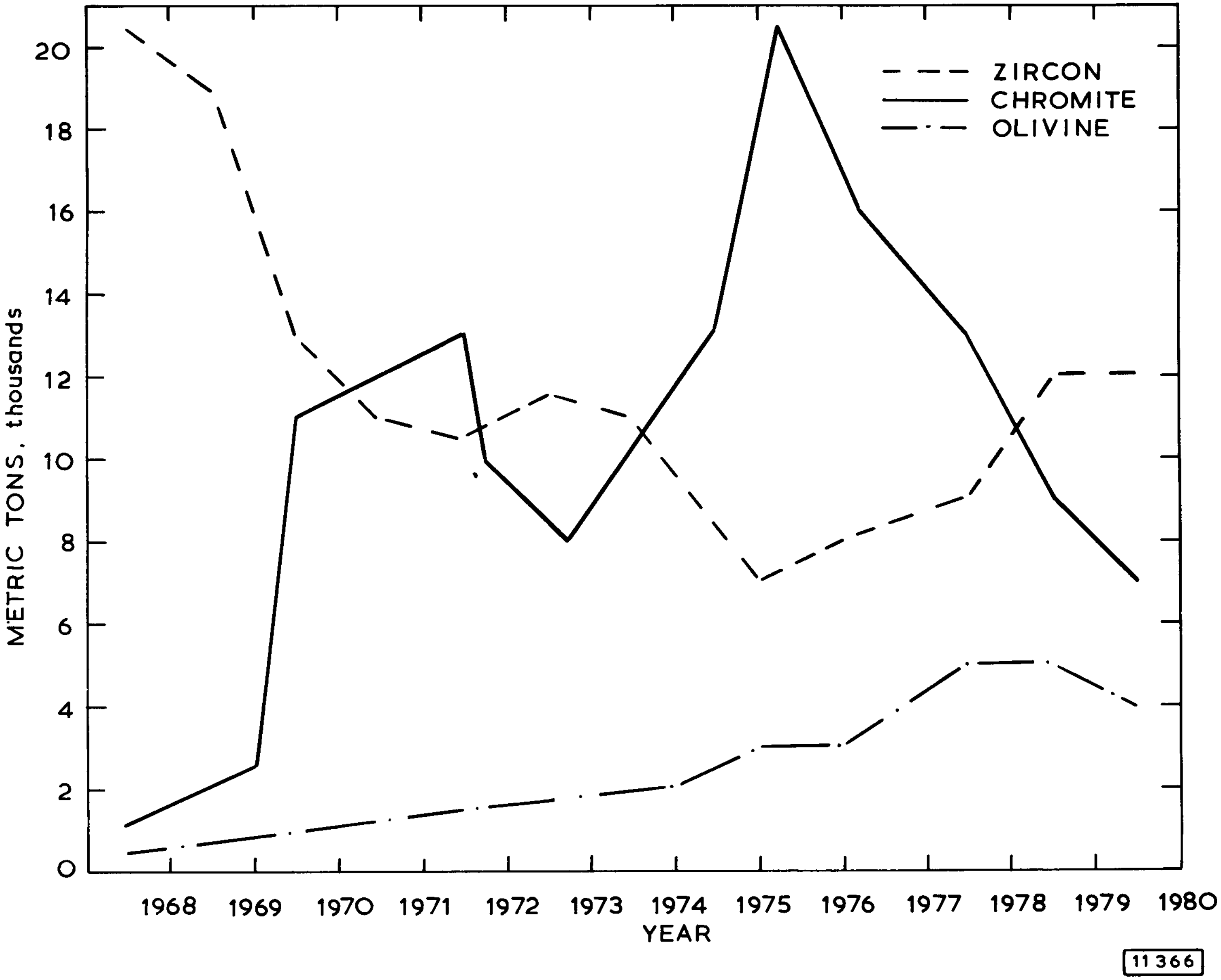

FIG. 10 REFRACTORY SAND CONSUMPTION IN U.K.

furnace campaign is finished or a process vessel becomes redundant the material in the lining may still have value. In the UK, for example, there are a number of reclaimers who sort, clean and process used bricks and incorporate the reclaimed refractory with fresh material for further service. In 1977 10% of the refractories in arc furnace sidewalls were reclaimed, but the chromite content is not known.

Reclamation of silica sands is often carried out[13], and reclamation of chromite and zircon sands would at first sight seem an even more attractive proposition because of their higher cost. Recovery is inhibited, however, by the need to separate the silica backing sand. When chromite alone is used as a facing sand more severe fusion occurs than is the case with chromite-zircon mixtures and the used chromite is less suitable for re-use.

Although chromite could be conserved by reclamation of used refractory bricks and foundry sands, the availability of adequate alternatives makes substitution a more attractive proposition. Larger total savings could be accomplished, and substitution would be less expensive and technically easier to accomplish.

## 5.8 Electroplating

### 5.8.1 Alternatives to Chromium

It is not easy to find a satisfactory electroplated alternative to decorative chromium plate. The only realistic substitutes are various alloy plating systems based on tin. These systems were developed for "barrel" plating of large numbers of small components, where the efficiency of chromium plating is often less than 10%. The chemical costs are much higher, but there are savings in labour costs in avoiding jigging of small components in a conventional plating bath. The alloy systems are not economically viable for large components, and there are other disadvantages also. The most widely used system is cobalt/tin, for which two commercial processes are available. One of these uses an acidic electrolyte containing fluoride, and this has given rise to effluent control problems. The other process uses cobalt and stannous salts in an alkaline solution containing an organic complexing agent which acts as a stabiliser[14]. This system appears to have become established as a possible alternative to chromium, although the deposit is darker, softer and less wear and scratch resistant. It has distinct advantages over conventional chromium plating for small components and complex shapes. Another alloy system is tin/nickel, but this is also based on fluoride, and produces a brittle, pink-coloured deposit. It has its applications[15] but is not really a satisfactory substitute for decorative chromium plate. In view of the fact that decorative plating cannot be considered to be a critical end-use, and that tin is also under consideration as a critical metal for which alternatives must be found, there is not a strong case for recommending R and D into the further development of these alloy plating systems.

There are several possible alternatives to hard chromium, although none is able to provide all of the desirable properties for which chromium is valued. Nickel can be deposited by chemical reduction, and in this way the difficulty of obtaining deposits of uniform thickness by electrodeposition can be overcome. Such electroless nickel coatings have been developed over the past 25 years for engineering applications. The standard process uses sodium hypophosphite as a reducing agent to deposit a nickel/phosphorus alloy containing 7-11% phosphorus. As deposited, the coating is not as hard as chromium, but it can be hardened by heat treatment to give a comparable hardness. There is a newer process which uses boron in place of phosphorus, and produces a coating with better high temperature hardness.

Electroless nickel coatings can be used as a substitute for hard chromium in many applications with complete success. There are some disadvantages: e.g. it is fairly costly, which is not so important for plating of a small number of articles, but in a repetitive process e.g. piston rings, jigging cost is lower per article plated and then the plating cost becomes relatively more important. The main disadvantage with nickel/phosphorus is the slow plating rate, and the general consensus of opinion is that the layer is not so wear resistant as hard chromium. An evaluation of the relative wear characteristics has been carried out by Tope et al[16]. In general it can be stated that electroless nickel is advantageous when plating complex shapes, or when only a few components require processing, while hard chromium is preferable where operating temperatures are high and a low coefficient of friction is important.

Another possible substitute for hard chromium is an electrodeposited heavy nickel layer. Natural deposition of nickel gives quite a soft coating, but this can be hardened by using doping solutions such as ammonium salts, some organic additives or nickel sulphamate.

A fairly recent development consists of electrodeposits of nickel or cobalt incorporating wear resistant materials such as carbides or alumina. Conventional electrolytes are used with the finely divided ceramic powder in suspension. The powder must be maintained in suspension by agitation of the solution, so that the process requires a greater degree of control than normal electrodeposition. Nevertheless the costs are reported to be of the same order as those of hard chromium plating[17]. Although chromium carbide is the most common ceramic in these deposits, many others have been used. A cobalt-based chromium carbide composite having excellent wear-resistant characteristics at temperatures up to at least 800°C has found extensive use in the aerospace industry[18], but these materials have not yet penetrated other markets. Metal-ceramic coatings can also be deposited electrolessly which has advantages for surfaces of complex geometry[19].

In applications where aluminium can be used a wear resistant surface can be imparted to the metal by hard anodising. Using a refrigerated sulphuric acid electrolyte (0-5°C) and voltages of up to 70 V a dense oxide film is produced. The hardness is about the same as electroless nickel deposits, but wear resistance is much better than might be expected from the hardness, and it has been claimed that a hard anodised aluminium bearing surface is as good as hard chromium[17].

The properties and applications of various possible alternatives to hard chromium are summarised in Table 25.

### 5.8.2 Conservation of Chromium

Losses of chromium in electroplating can be reduced either by development of higher efficiency plating processes or by recycling. Technology is under development in both these directions, but the plating industry is conservative and commercial acceptance of new processes is not easy to achieve.

#### 5.8.2.1 Alternative Processes

Trivalent chromium plating is an alternative which offers several important advantages over conventional hexavalent chromium baths. The technology is reviewed in detail in the Dutch report (Appendix B). Chromium consumption is reduced because plating can be carried out from a much more dilute solution, and consequently spray and drag-out losses can be as much as an order of magnitude smaller. Another important advantage is that the throwing power is much better, so that the deposits are much more uniform in thickness and complex shapes can be plated more easily. Current interruptions, which cause problems in hexavalent plating have no adverse effect. Also, trivalent chromium is far less toxic and posses fewer health and safety problems in the factory and in disposal of the effluent.

Despite these distinct advantages, trivalent chromium plating has only achieved limited commercial acceptance. There are two commercially available systems for decorative plating. One is a wholly inorganic solution developed by the British Non-Ferrous Metals Research Association (BNF), and the other, more successful one is a solution developed by Albright and Wilson[20] which uses an organic complexing agent for the chromium. An important disadvantage of all trivalent baths is that at the present time it is not possible to get a thick enough layer for engineering purposes because the deposit loses coherence as it gets thicker. Its use is therefore restricted to decorative plating, and hence the darker colour of the deposit has met with market resistance. It should be emphasised, however, that the question of whether the colour is more or less attractive than that of conventional chromium deposits is a subjective one. The baths are more difficult to control, and therefore good housekeeping and analytical control problems are greater than many plating companies find acceptable.

TABLE 25. - Comparison of Principal Wear-Resistant Coatings

| Coating | Hardness as deposited (HV) | Range of usual finished thickness, µm | Characteristics of coating | Typical Applications | Approx. relative cost |
|---|---|---|---|---|---|
| Hard Chromium | 900 | Up to 200 sometimes to 500 | Hard wear resistant coating having low frictional co-efficient and non-stick properties. Resistant to corrosion. Brittle, not resistant to shock. | Gauges.<br>Cutting tools.<br>Metal forming and drawing dies. Building up worn parts. | 3 |
| Heavy nickel | 200 to 400 | Up to 500 | Softer wear-resistant coating, also withstands corrision and fretting attack as well as heat scaling. Can be finished by turning. | Hydraulic equipment.<br>Food processing equipment.<br>Building up worn parts. | 1 |
| Electro-less nickel | 500 (1000 on hardening) | 10 - 50 | Resistant to wear and corrosion and uniform in thickness. Can be applied without using complicated jigs and anodes. | Plastics moulds.<br>Textile machinery<br>Hydraulic valves.<br>Ball valves. | 4 |
| Metal ceramic composite (based on nickel or cobalt) | 400 to 500 | 50 - 125 | Resistant to extreme wear at elevated temperatures. | Compressor blade roots.<br>Water pump thrust washers. Rotary engine castings. | 5 |
| Hard anodising of aluminium alloys | 500 to 600 | 25 - 75 | Coating formed from outer layers of workpiece by anodic action. | Water pumps<br>Disc brake cylinders.<br>Hydraulic pistons. | 2 |

1 = least costly

5 = Most costly, but the order of merit is for approximate guidance only as the costs depend upon so many factors, such as the shape of the work and the volume of the production, notably for electroless nickel coatings.

Source: Reference 17

Also the conventional process is very robust and will stand the presence of metallic impurities, while trivalent baths are very susceptible to impurities. The cost of chemicals is higher, but effluent treatment should be cheaper, and jig loading can be increased. Overall it is claimed that the method can be more cost effective, especially for plating complex shapes.

If it were possible to develop a trivalent hard chromium plating process substantial energy savings could be made. On valency considerations alone electricity consumption would be half the amount used in the hexavalent process, and on the basis of past experience an improvement in current efficiency could also be expected. In addition to improvements in the efficiency of chromium deposition, there would be prospects of further chromium savings because at the present time it is necessary to grind back to size hard chromium deposits because of the uneven deposit from hexavelent chromium baths.

Chromium conservation can also be promoted by improving the corrosion resistance, and therefore extending the lifetimes, of hard chromium plated components. The problem is to overcome the risk of corrosion caused by macro-cracking of the deposit without adversely affecting the resistance to mechanical wear. Some work has been carried out on satisfying these requirements by "double hard chromium plating"[21]. In this technique a thin crack-free layer of less than 10 µm is deposited underneath a much thicker microcracked coating of about 50 µm thickness. This topic is also discussed in detail in the Dutch report.

Vacuum deposition processes such as ion plating should be much more efficient in the use of materials than electroplating. Ion plating is capable of producing highly adhesive films with good uniformity and grain structure[22]. It is possible to produce films of any metal or alloy and hard coatings of refractory metal nitrides and carbides. The dimensions of the vacuum chamber limit the size of components which can be treated, but chambers as spacious as 3 m long and 2 m diameter are currently operational in the USA. Capital investment is high, however, and, because of the batch nature of these processes, it is difficult to envisage successful competition with the high throughput plating industry.

#### 5.8.2.2 Recycling

Recycling of drag-out solution can be carried out by using a counter-current rinsing system and some method of concentrating the solution for return to the plating bath to replace evaporation losses. The simplest method is to concentrate the solution by evaporation. This is done in a process developed by Corning in the USA[23]. The equipment includes a rising film evaporator in which a very fast rate of heat input into a thin film of the solution is achieved, thereby minimising solids precipitation or crystallization on the heat exchanger surfaces. The system operates under reduced pressure to lower the boiling point of the solution. Using this method, chromium losses in a large decorative plating plant in the UK have been reduced to 5%. The capital cost of the plant was recovered in 11 months of operation, in reduced chromic acid consumption and savings in effluent treatment costs. The drawback of this system is that it also concentrates impurities, but in practice this has not caused any problems and no build-up has been observed of metals such as iron, copper, nickel or trivalent chromium. If accumulating metal impurities are likely to be a problem a cation exchanger can be used for purification of the recovered chromic acid.

Alternatively selective methods of concentration such as reverse osmosis or electrodialysis can be used for chromium recovery. A lot of development work is still needed on membrane systems and reduction of energy consumption. An electrodialysis system is described in the Italian report (Appendix A).

In all the member countries the electroplating industry includes a large number of small "jobbing" platers. High technology approaches to reducing wastage are not appropriate here because of the lack of capital to invest in recycling processes. An alternative solution is to collect the sludges from pollution control system for centralised recovery of metals. In Italy Fiat has studied this concept and developed a hydrometallurgical process for recovery of copper and chromium from sludges,

(Appendix A) and centralised treatment has also been investigated by Warren Spring Laboratory for application in the Birmingham area of the UK.

In the UK the first step was to carry out a detailed survey of wastes in a region where the metal finishing industry is highly concentrated. This survey was carried out by Warren Spring Laboratory in cooperation with the West Midlands County Council and the Severn Trent Water Authority. Samples of sludges were collected for analysis and estimates were made of the quantities of metals in the wastes in the area surveyed. The survey indicated that in a clearly defined area of about 100 square miles to the west of Birmingham about 170 tonnes/year of nickel, 140 tonnes/year of copper and 226 tonnes/year of zinc could be recovered as metals or salts from these wastes. The sludges also contained about 150 tonnes/year of chromium, but recovery of this metal was not considered to be economically attractive because of the need to separate chromium from iron. In the event of a shortage, however, no doubt recovery of this chromium would be attractive.

It was estimated that a centralised plant to treat these wastes would cost about £2 millions, excluding land, and assuming that capital was available at 12% the process could break even if a charge of £10/tonne were made for disposal of the wastes. The value of the recovered metals would be of the order of £800,000 at mid-1979 prices.

## 5.9 Leather Tanning

### 5.9.1 Alternatives to Chromium

Many metals have been tested for their tanning capacity, but in fact very few are satisfactory and none is as good as chromium. Aluminium and zirconium seem to be the most suitable possible substitutes, iron has been used but is much less satisfactory because of a tendency towards staining. Aluminium tanned leather tends to revert when wet and is degraded by perspiration, while zirconium is initially very good but suddenly de-tans. The tanning industry has expressed some interest in aluminium tanning, because it has a significant advantage over chromium in that a white tannage is produced. So far no satisfactory system has been developed, although there is some limited commercial application of re-tanning vegetable tanned material with aluminium in the UK but this only amounts to about 0.5% of production. There is interest in the use of aluminium tannages in several leather research centres in the Community. CSIRO in Australia have done some work on chromium and zirconium combinations with a view to reducing chromium consumption. It appears that the USSR may be furthest ahead in zirconium tannage but linguistic problems make it difficult to monitor their work with any precision. There is a textbook on zirconium tannage published in Russian in 1972; a translation into a more familiar language would be useful.

Various synthetic substitutes for leather have been introduced, but their success has been limited to ladies' fashion shoes. The attempt by Dupont to introduce a porous PVC substitute called Corfam a few years ago is well known, but this was not a commercial success and the process was sold to an Eastern European country. No synthetic material has yet been able to fully reproduce the desirable qualities of leather, particularly for men's shoes. Also there has not been a sufficient price differential between leather and synthetic materials to encourage substitution. It has to be admitted that it is possible to make synthetic materials which are more uniform in properties, and it is, therefore, possible that in the future a more successful substitute material could be found.

### 5.9.2 Chromium Conservation and Recycling

There are substantial losses of chromium in effluents from the single bath tanning processes. Efficiencies of chromium uptake vary from company to company according to the details of the process used and the thickness of the hides, but on average losses of about 25% appear to be representative of the industry in most countries.

A comprehensive study of methods of reducing chromium wastage in the tanning industry has been carried out by the British Leather Manufacturers Research Association (BLMRA). Case studies were carried out in tanneries which had installed systems to recycle spent liquor to the main tannage. It was found that the average chromium saving in five bovine leather tanneries was 15%. In two cases the total operating costs (with capital investment depreciated over 5 years) were compared with savings in chemical costs. There were great differences between the two cases in size and type of operation, but there was an overall saving of about £1 per tonne of limed hide during the first 5 years. Thereafter the net savings in processing costs should continue to improve when the capital investment has been written off and the price of chromium chemicals continues to rise.

The alternative method of re-using the chromium content of spent tanning liquor is by precipitation of the hydroxide, separation of the solid and re-dissolution in acid for a subsequent tannage. BLMRA have confirmed the findings of TNO[24] in Holland that magnesia is the most attractive precipitant for this purpose. Pilot scale experiments in four UK tanneries were very successful, showing that magnesia produces a dense, easily dewatered precipitate and leaves low residual concentrations of chromium in the supernatant liquor.

The general conclusion from this work is that recycling of spent tanning liquors can quite easily increase the chromium uptake to 80-85%, and that there is an economic incentive to do so. It is feasible to achieve 95% uptake but the plumbing cost would be high. Some companies have already increased their efficiency of chromium use, but it needs capital investment and this may inhibit progress in other areas. The alternative method of precipitation of chromium hydroxide for subsequent re-use also looks attractive, but commercial application is at an earlier stage of development. In either case there does not appear to be a requirement for much further R and D.

An alternative method of chromium tanning, in which it is claimed that the chromium uptake is as high as 98%, has been developed by Garverforsøgstationen in Copenhagen on behalf of the Nordic Leather Research Council[25]. The technical details are confidential, but the method is based on "know-how", using commercially available chemicals in conventional equipment. It is used on a routine basis in seven Scandinavian tanneries and in a tannery in another EEC country[26].

## 5.10 Pigments

### 5.10.1 Alternatives to Chromium

The high toxicity of both lead and hexavalent chromium has led the paint and pigment industries to consider and use a large number of alternative pigments, particularly organic azo compounds, which are much less toxic. Some properties of a number of alternatives to lead chromate are summarised in Table 26.

Alternatives are available for all colours, and the main loss in moving away from inorganic pigments is in opacity. There is also a cost penalty, but not necessarily as severe as the relative prices in Table 26 suggest because the cost of pigment in a specific finish depends on shade and tinting strength.

Finding a substitute for a chromate pigment for a particular application which is satisfactory in all respects might be quite difficult; a study of pigments for automotive finishes in the USA was able to recommend only 13 out of 79 pigments listed as being potentially suitable for this purpose[27]. The use of chromates in the passivation of zinc plated or galvanised surfaces would also be difficult to replace. Phosphate treatments are sometimes used, but they do not give the same resistance to surface corrosion. Nevertheless new pigments are continually developed by the chemical industry, and there appears to be no real need for additional R and D in this area.

TABLE 26. - Alternative Pigments to Lead Chromate

| Chemical Type | Shade | Opacity | Durability | Approximate Price (relative to lead chromate) |
|---|---|---|---|---|
| Inorganic | | | | |
| lead chromate | bright | high | moderate-high | 1 |
| yellow iron oxide | very dull | high | high | 0.25 |
| nickel titanate | low intensity | moderate | high | 2-3 |
| cadmium sulphide | bright | high | moderate | 4-8 |
| Organic | | | | |
| arylamide | bright | low-moderate | moderate | 4-7 |
| disazo, benzidine | bright | low | low | 6-8 |
| condensed azo | bright | moderate | moderate-high | 20-25 |
| flavanthrone | dull | low | high | 40 |

## 5.11 Timber Preservation

Alternatives to the CCA preservatives exist (e.g. creosote, metal naphthenates), but they are less cost-effective because the guaranteed lifetime of the treated wood is shorter. The CCA compounds can be fixed without chromium, but the cost would be higher. Research into alternatives to CCA is being carried out in industry, motivated largely by concern about the use of arsenic, but the effectiveness of alternatives has not yet been proven in the field.

## 5.12 Corrosion Inhibitors

There has been some decline in the use of zinc/chromate inhibitors because of the high cost of chromate removal from the cooling tower blowdown. The most successful alternatives is a zinc/phosphonate inhibitor containing 4-6 g/m$^3$ zinc and 10-30 g/m$^3$ phosphate, the concentrations depending upon the hardness of the water. The use of zinc/polyphosphate is less popular because of the possibility of reversion to orthophosphate and the subsequent precipitation of calcium phosphate.

# 6. CRITICALITY

Criticality is difficult to define precisely but for the purposes of this study it is seen as a measure of the technical and economic impact on specific end-uses of the non-availability of chromium and the significance of these end-uses for the economy as a whole. It is therefore a rather complex concept involving *inter alia* market share, importance of application, and difficulty in finding an alternative. It is important to distinguish between criticality and vulnerability, which as indicated in Chapter 2, is related to potential threats to the supply of chromium-bearing raw materials to the Community. Materials such as chromium, tungsten, silver and tin were chosen as subjects for case studies because they were perceived to be highly vulnerable. It is beyond the scope of this report to discuss the political reasons for this decision, but rather to accept that a degree of vulnerability exists and to decide which end-uses are the most critical. Only in this way can priority topics be identified for inclusion in a research programme.

There are a number of important aspects to criticality which can be discussed qualitatively, although it is not possible to compare their relative importance in rigorous economic terms. Perhaps the easiest to appreciate are the purely technical considerations which were discussed in the previous chapter. For example, adequate alternatives to chromite are available in most of its refractory applications, and the price structure is such that a considerable degree of substitution has already taken place. Similarly chromium could be largely eliminated from engineering steels, although there would be a substantial cost penalty, and reasonably satisfactory alternatives exist in many of the chemical applications. Such applications cannot be considered to be critical in the context of the present study.

The situation is less straightforward in the applications having requirements which cannot in the foreseeable future be satisfied by chromium-free materials. In these circumstances other factors such as market share, impact on employment, environment etc. must be brought to bear on making judgements. Stainless steels are the biggest single user of chromium, accounting for just over half of Community consumption. Although chromium cannot be eliminated, there are possibilities, albeit rather long-term ones, of reducing the proportion needed in some alloys. Because of the large market share, quite small reductions in the proportion of chromium used could result in large savings in consumption. Not all uses of stainless steel, however, can be regarded as critical. If it is assumed that the UK consumption pattern is reasonably representative, then one third of stainless steel production is used in process plant and power generation. These are basic industries, of vital importance to general economic activity, and therefore availability of chromium is highly critical. On the other hand a large proportion of chromium demand goes into applications which are by no means essential, and are open to substitution without much technical difficulty or expense. Indeed many of these uses have developed as a result of the kind of commercial efforts to penetrate new markets which were mentioned at the beginning of Chapter 5. Examples include the stainless steel used in many consumer goods, catering equipment and transport. It is difficult to put a precise figure on the amount involved, but possibly 30-50% of the consumption of stainless steel could be sacrificed if a serious emergency required that chromium should be conserved for more critical uses.

There are other applications which use relatively small quantities of chromium but are no less important to a wide range of industries. Examples include hard chromium plating, tool steels, and high performance alloys, each accounting for only a few per cent of consumption. Because of the small quantities involved it would be reasonable in a crisis to divert chromium saved elsewhere into these critical applications if substitution proved to be very difficult. This would be the case for tool steels and superalloys, and it would be sensible to concentrate R and D efforts on other areas where success is more likely.

It is possible that any pressure on chromium supplies might not apply equally to ferroalloys and chromite ore. Because of inadequate ferroalloy capacity within the Community any shortfall in supplies would have to be met by savings in the metallurgical sector even if chromite were still available. Similarly a situation can be envisaged in which the chromium needed for hard surfacing would have to be provided by savings in other chemical end-uses. Thus chromium saved by sacrificing a non-critical application might not be available in a form suitable for use in a more critical one, and it would be wrong to reject R and D in applications such as electroplating or leather tanning simply because the consumption of chromium is relatively small. Potential savings might be of the same order as in more obviously critical applications, and the chromium saved could be used, for example, in hard plating or the manufacture of superalloys. In a sense criticality is a double edged concept because in the field where the largest savings in chromium might be possible much of the saving could be realised simply by sacrificing the application, while in the really indispensable applications research could confer much greater benefits by relieving the pressure on critical industries, but the savings would be smaller.

The remaining uses of chromium, e.g. decorative chromium plating, leather tanning, pigments, are less obviously critical and no doubt could be sacrificed to a large extent if circumstances demanded it. Nevertheless it cannot be denied that disruptions in chromium supply would have a strong impact on the industries involved, and there could be serious social consequences. Also, though not strictly related to criticality, there are environmental factors which cannot be ignored.

The effects of a chromium shortage on employment are not easy to assess. Table 27 provides data on the numbers of employees in the primary chromium-using industries in the Community. The total of just under 2.8 million is about 10% of employment in all manufacturing industries. Not all these employees will be involved in chromium-containing products. In Italy, for example, it is estimated that only 3% of workers in the steel industry and 8% in the refractories industry handle chromium (Appendix A). It is not possible, using published statistics, to make an estimate of the numbers of employees in the user-industries who are directly involved with chromium-bearing materials (e.g. stainless steels and other alloys, leather, pigments etc.) The only real conclusion that can be drawn from employment statistics is that they confirm the relative importance of the metallurgical applications.

TABLE 27. - EEC Employment in Chromium-Consuming Industries, 1973

| NACE Classification | Industry | Employees thousands | Employees % |
|---|---|---|---|
| 22 | Production and Primary Processing of Metals | 1655.9 | 60 |
| 248 | Manufacture of Ceramic Goods | 332.2 | 12 |
| 311 | Foundries | 354.2 | 12 |
| 313 | Secondary Transformation, Treatment and Coating of Metals | 356.4 | 13 |
| 441 | Tanning and Dressing of Leather | 76.8 | 3 |
| Total | | 2765.5 | 100 |

Source: Eurostat Quarterly Bulletin of Industrial Production 3-1976.

Finally it is relevant to consider briefly the adverse environmental impact of the use of chromium. This really only applies to the chemical applications, and needs to be taken into account as a factor in making recommendations for R and D only in the cases of electroplating and leather tanning. Electroplating conventionally uses chromium in the hexavalent state, in which it is highly toxic, and wastage in the industry is high. Techniques are available for recycling effluents, or reducing the chromium to the much less toxic trivalent state, but the hazards involved in handling chromic acid are not eliminated. This problem does not arise in leather tanning, which mostly uses trivalent chromium solutions. If it were decided that tanning was not a critical use of chromium which could be sacrificed in a crisis, a very considerable waste disposal problem would be created in the form of useless hides. Another point worthy of consideration is that leather is a renewable resource indigenous to the Community, whereas synthetic substitutes are oil-based. The industry therefore has an importance which is not reflected in its relatively small market share.

To summarise, there is no doubt that stainless steels, in at least 50% of their end uses, are highly critical materials with a fundamental importance to a wide spectrum of industries. Other chromium-containing alloys, such as tool steels and superalloys, can also be regarded as critical materials, but because of their small market share and the difficulties of substitution, maintenance of chromium supplies to these end-uses is regarded as essential. The refractory applications of chromite are important, but not critical because most of the chromite used could be replaced by alternative materials on the basis of present knowledge. For various reasons the criticality of electroplating and leather tanning is greater than is apparent from their market shares, and a search for substitutes is highly desirable, although less important than in the stainless steel sector.

# 7. CONCLUSIONS AND RECOMMENDATIONS

## 7.1 Potential Savings of Chromium

Four methods of reducing the Community's chromium consumption can be recognised. The first is to carry out long-term R and D leading to technologically acceptable substitute materials containing either no chromium or a substantially smaller proportion of chromium. This would be the basic aim of a Community R and D programme. Secondly, there is the possibility of substitution without loss of performance on the basis of existing knowledge, with little or no requirement for R and D although possibly there might be a substantial cost penalty. Recycling of chromium-bearing wastes offers prospects for making small savings, particularly in the chemical applications sector. Finally non-critical end-uses could be sacrificed and replaced by lower-grade and less convenient but nonetheless adequate alternative materials. Estimation of the quantities of chromium which might be saved by these methods is very difficult, and the following is no more than a very rough guide to the maximum savings that might be achieved, based upon the discussion in Chapters 5 and 6.

Reduction of the chromium content of stainless steels, while retaining adequate performance characteristics, would require long-term R and D. Assuming a successful outcome to such research, it seems possible that around one third of chromium consumption in these alloys could be saved. Alternatively sacrificial substitution (i.e. using polymers, aluminium, mild steel with surface coatings etc.) in non-critical applications could possibly save up to 50% of consumption. This could be done on a shorter time-scale, but at the expense of substantial industrial disruption. Chromium could be largely eliminated from engineering steels using existing knowledge, although no doubt the changes would take considerable time to implement. Based on American estimates[4] perhaps 80% of chromium consumption in these steels could be saved, but there would be a cost penalty. Substitution for chromium in tool steels, superalloys and other high performance alloys is not regarded as a realistic possibility.

There are already significant trends towards the replacement of chromite in its refractory uses, and if necessary a 90% saving could probably be made. This could be achieved with little or no research effort; there might be a cost penalty, depending on the relative price fluctuations of the alternative materials.

In electroplating, a 70% reduction in consumption could be achieved by elimination of wastage; in the case of decorative plating this could be facilitated by adoption of trivalent plating baths. Hard chromium plating is regarded as a critical end-use and substitution would not be easy. Some chromium conservation seems feasible by improving the corrosion resistance of the coating and the use of electrodeposited composite coatings of nickel with ceramic materials also seems promising. Potential savings are difficult to estimate, but they would be unlikely to exceed 30% of chromium consumption in the electroplating industry. Chromium could conceivably be wholly replaced by metals such as aluminium and zirconium in leather tanning, although it is perhaps unlikely that complete elimination of chromium would ever occur. Approximately 20% reduction in consumption could be achieved by improving the extent of recycling of tanning liquors. All these developments would require R and D, fairly short-term for reducing wastage, but successful substitutes would require a 5-10 year period of development.

Chromium used in miscellaneous chemical applications such as pigments, wood preservatives etc. could be sacrificed or replaced by more or less inferior or expensive alternatives.

The potential savings of chromium are summarised in Table 28. It is emphasised that the boundaries between the four methods of conservation are not well defined, and in some cases they are mutually exclusive. There are, however, some useful observations that can be made. Successful attempts to substitute for chromium in stainless and engineering steels would save as much chromium as the sacrifice of non-critical applications, and might in a crisis avoid the adverse impact of such sacrifice on industry. Encouragement of recycling in the electroplating industry seems capable of saving more chromium than substitution, but the opposite is true in leather tanning.

TABLE 28. - Potential Annual Savings in Chromium Consumption

| End-Use | tonnes of chromium | | | |
|---|---|---|---|---|
| | Substitution after successful R and D | Elimination of wastage | Substitution involving present knowledge | Sacrificial substitution |
| Stainless Steels | 90,000 | - | | 130,000 |
| Engineering Steels | - | - | 40,000 | - |
| Refractories and Foundry Sands | - | - | 54,000 | - |
| Electroplating | <4,500 | 10,000 | - | - |
| Tanning | 40,000 | 8,000 | - | - |
| Miscellaneous | - | - | - | 25,000 |

Indeed the possible savings that could be achieved if research into alternative tanning systems were successful is very high in relation to its market share. The overall outcome of a successful R and D programme would be a 25% maximum saving in chromium consumption in the Community. In addition substitution on the basis of present knowledge and some sacrifice of non-essential uses could increase the potential savings to 50%.

## 7.2 Proposals for a Research and Development Programme

There is a danger that the figures mentioned in the previous section might give the impression that substantial reductions in chromium consumption will be easy to achieve. This is not the case. The inescapable conclusion of the discussion in Section 5.1 is that it is very difficult to force substitution to take place even when alternative materials with attractive properties are available. Chromium is difficult to replace in many of its applications and where this is the case the short term prospects for finding satisfactory substitutes are poor. In the longer term (say 10-20 years) it is possible that some progress might be made, but R and D will need to be carried out at a fundamental level, and close scrutiny of projects will be necessary to ensure that the aim of eventual industrial application is kept in sight. To be realistic the probability of success is not high and it is suggested that the budget for an R and D programme should be modest. Another important point which is emphasised is that it is not rational to suggest reducing Community dependence on one vulnerable material by trying to promote new uses for another one which is also deemed to be at risk. This means that substitution of such metals as cobalt, tungsten and tin for chromium should not be encouraged.

After careful consideration of all the factors involved there are several areas where it has been decided not to recommend R and D. These are listed below, with the reasons for their rejection:

### 1. Engineering and Tool Steels

Considerable substitution for chromium in engineering steels is possible using other carbide forming elements, although there would be a cost penalty. Sintered carbides could be used in place of a high proportion of tool steels. These materials use cobalt as a binder, but nickel could be used in its place. The potential for saving chromium in these steels is small and it would be better to concentrate efforts in other areas.

### 2. Superalloys

These materials have been energetically developed and few promising lines of research remain unexplored. Industry is deeply engaged in this work and the prospects for making a significant impact seem small. Also there are important military applications, and this is a region the Common Research Policy does not cover.

## 3. Refractories

With the decline of the open-hearth furnace consumption of chromite refractories in the steel industry has decreased, and further reductions in demand can be expected as a result of trends taking place in the electric arc-furnace. Zircon could replace chromite foundry sands, although chromite gives better steel castings provided the quality of the ore is good. In general satisfactory substitutes appear to be available in the refractories field and this is not considered to be a priority area for R and D.

Experimental R and D programmes are recommended in three fields viz stainless steels, electroplating and leather tanning. It will be necessary to discuss stainless steels with representatives of DG III, and it is also recommended that National Delegations to the Working Group should consult the relevant industries in their own countries, because within the scope of this study it has only been possible to seek the views of a very small sample of companies.

The research proposals are as follows:

## 1. Stainless Steels

Complete replacement of chromium in alloys is not generally possible without unacceptable loss of performance, but there is some scope for reducing the amount required to reach a desired specification. For example there has been some work in several countries on reducing the chromium contents of stainless steels from 18% to 12-14% by adding aluminium, silicon or rare earths. Resistance to high temperature oxidation can be maintained at lower chromium contents, although other aspects of performance are sacrificed. There is also a case to be made for fundamental work on the reasons for the 12% minimum chromium content which is considered necessary for resistance to both high temperature oxidation and wet corrosion. It is clear that this is due to the formation and breakdown of protective films which is limited, not by thermodynamic stability, but by the kinetics of diffusion within the alloy and by the defect structure of the oxide film. Basic research is recommended in this area, paying particular attention to the way in which the structure and properties of the film are modified by additions of silicon, aluminium, rare earths, mechanical working, and by surface treatments e.g. with boron, borates, silicates and phosphates. Invitations for research proposals should be broadly drafted so as to encourage novel ideas, and scrutinised by experts who would assess the probability of a successful outcome to the research leading to the formulation of new alloys of lower chromium content and adequate performance characteristics related to specified user requirements.

It seems very likely that low chromium steels can be developed with equivalent high temperature oxidation resistance to the standard grades currently in existence. Such a development should be feasible within, say, 10 years because this type of work is currently being pursued in several countries. Where the difficulty lies is in developing a composition that can be produced by bulk steelmaking techniques and that has good fabricability i.e. weldability and formability. This is vital to the successful development of a material suitable for commercial use, but is sometimes overlooked by alloy developers. It can take just as long, or longer, to achieve these attributes as it does to develop the basic composition to resist an environment.

The prospects for success in producing low alloy wet corrosion resistant steels seem poorer. Most research on wet corrosion appears to be moving towards the development of even higher chromium contents in both ferritic and austenitic steels.

Introduction of new alloys is made difficult by the need for adequate performance tests and lead-times are long. The possibility for introducing concerted action on performance testing, such as exists in the field of gas turbine materials under COST 50, should be explored.

## 2. Electroplating

There is obviously scope and environmental pressure to reduce wastage in the chromium plating industry. One way of improving the efficiency of chromium usage is to use a trivalent chromium electrolyte. There are commercial systems available, but there are disadvantages, including instability of the electrolyte, high costs and market resistance to the colour of the deposit. Health and Safety considerations are the main justification for research in this area, although it should be possible to reduce chromium losses in drag-out solutions. On behalf of The Netherlands, TNO wish to recommend research into trivalent chromium plating with the aim of making the method more attractive to industry. Efforts to use trivalent baths in hard chromium plating have not yet been successful, and some experts in the field believe that the prospects for future success are not good. Nevertheless, in view of the critical nature of this application, this would be a worthy long-term aim of the research, and new ideas should be encouraged.

Although hard chromium layers are very resistant to wear there is room for improvements in corrosion resistance. There is evidence to suggest that this can be done by deposition of double layers and, by extending the lifetime of hard chromium deposits, lead to conservation of chromium in this important application. At the request of The Netherlands, research is also recommended on this topic, but it is also suggested that novel proposals for the development of alternatives to chromium should be encouraged. Nickel deposits incorporating wear resistant materials would seem to be a particularly promising area for further research, whether deposited electrochemically or by electroless methods.

## 3. Leather Tanning

Leather tanning is an important industry in two respects which seem relevant to this study. It offers an outlet for hides which would otherwise pose a considerable waste disposal problem. Secondly it is a renewable resource indigenous to the member countries, whereas synthetic substitutes are oil-based, and in any case they do not fully reproduce the desirable properties of leather. Long term research into the fundamental chemistry of the tanning process could improve the results obtained with metals such as aluminium and zirconium so that a satisfactory substitute for chromium-tanned leather could be found. There would be other advantages particularly in the absence of colour in the tannage, and research in this field is recommended.

The suggested budget for an indirect action programme is 4.1 mua over a period of 5 years, of which it is expected that the Commission would provide a contribution of 50%. It is proposed that the funds should be allocated as follows:

| | |
|---|---|
| Stainless steels | 2.5 mua |
| Electroplating | 0.8 mua |
| Leather tanning | 0.8 mua |

These figures do not include the cost of a concerted action programme on performance testing.

## 7.3 Suggestions for Further Study

### 7.3.1 Recycling

Losses of chromium in effluents are substantial in the electroplating and leather tanning industries, and conservation could be achieved by promoting recycling in these industries. It is suggested that the Non-Ferrous Metals Working Group should be asked to give consideration to the opportunities available. In particular they should investigate counter-current rinsing and methods of concentration of chromic acid in the plating industry. Methods such as evaporation, reverse osmosis and electrodialysis would be appropriate for larger companies, while the centralised treatment of sludges could help the smaller "jobbing" platers. Of course, such methods are also available for the recovery of other metals, and chromium cannot be considered in isolation.

### 7.3.2 New Materials

Italy has suggested studies of ceramic materials, polymers and fibreglass-reinforced resins as substitutes for chromium-containing alloys. The possibilities for substitution are not restricted to chromium, however, and this opens up a new field of study requiring information from sources not covered in the present work. It probably requires the construction of a property/consumption matrix for specific materials so that substitution can be approached logically and priorities for R and D can be assigned objectively. In other words metals, alloys and surface finishes would be characterised according to their physical and chemical properties, price and tonnages used. The relative importance of new materials could then be judged by their position in such a matrix. A similar method might be used to assess the potential of surface coatings, cladding etc. in the conservation of alloying elements.

It is suggested that a case study might be carried out along these lines to enable the potential of new materials to replace vulnerable metals to be assessed. The recent proposal for a council decision on the adoption of a programme of research in the field of clay minerals and technical ceramics contains some relevant research ideas, so that the need for co-ordination is obvious.

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COMMISSION OF THE EUROPEAN COMMUNITIES
(Directorate General XII - Research, Science and Education)

APPENDIX A to WSL Report

# CHROMIUM SUBSTITUTION STUDY

Report for Italy

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## 1) Introduction

Chromium and chromium-bearing materials are vitally important commodities to industry in the EEC.
The Community's vulnerability lies in the fact that 98% of the reserves of chromium ore are situated in politically sensitive areas (USSR, South Africa and Rhodesia).

As far as end use is concerned the breakdown is broadly in three categories:

Metallurgical
Chemical and Foundry Sands
Refractories

The purpose of the study is to investigate whether or not a Community R & D programme might be capable of producing alternatives applicable to important end-uses of chromium. The first stage consists in the interpretation of the available data, on consumption and end-use patterns. Known substitute materials shall be identified and the economic and technological impact of such substitution shall be discussed. The information will be used to define critical end-uses, and R & D proposals will be aimed at developing new substitute materials for critical applications.

Clearly, there are difficulties in deciding the degree of importance attached to the end products as measured

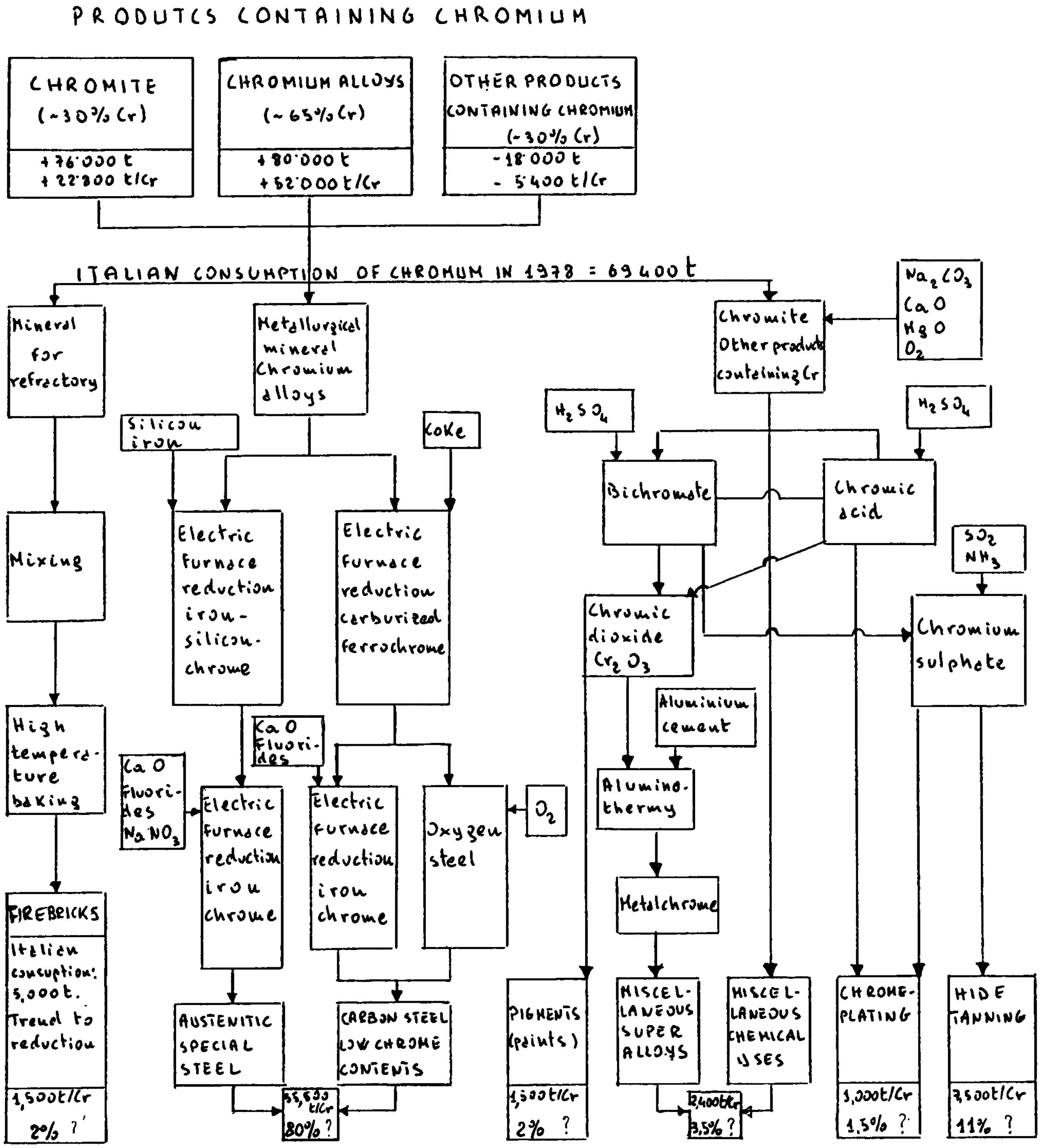
by profitability, added value, employment, balance of payments, future opportunities etc.
The intention, therefore, is to define scenarios arising from absence or shortage of supply without, necessarily, comparing their relative importance in rigorous economic terms.

Chromium production in the world in 1972-73 was 3.3 millions of tons of chromite ($Cr_2O_3$) per year. The breakdown per producer countries was:

| | |
|---|---|
| - USSR | 800,000 tons |
| - South Africa | 700,000 tons |
| - Albania | 280,000 tons |
| - Rhodesia | 270,000 tons |
| - Turkey | 260,000 tons |
| - Philippines | 230,000 tons |

## 2. Main uses of chromium in Italy

The main uses of chromium are the following:



The main chromium mineral is chromite [iron and magnesiumaluminium chromium = $(Fe, Cr, Al)_2O_3$ $(Mg, Fe)O$]
There are three main types of mineral

| CHROMIUM CONTENTS % | $Cr_2O_3$ CONTENTS % |
|---|---|
| METALLURGIC CHROMITE 33% | 48% |
| CHEMICAL CHROMITE 30% | 45% |
| REFRACTORY CHROMITE 25% | 36% |
| AVERAGE MINERAL CONT. 31% | - |

As shown in the above table, from chromium ore end products containing chromium are obtained (stainless steel or alloy steel, refractories, paints, tanned products, chromate products, etc.) using intermediate products (ferroalloys with chromium, bichromate, chromic acid, etc.). The production of these intermediate products involves losses, as indicated in the table hereunder, which must be considered for a clear picture of chromium consumption:

| end use | intermediate products | % loss | remarks |
|---|---|---|---|
| steels | ferroalloys with chromium | variable up to 20% | loss in fumes as dust |
| refractories | mixing | 5% | dust |
| chemical uses | bichromate | 15÷ 20% | 8÷ 10% in sand waste (sand); the remainder in waste water |

There is to add to these losses the losses resulting from the change from intermediate products to end products, as shown in section 5.2

## 3) Consumption of Chromium in Italy

- Consumptions of ore chromite were:

| year | 1969 | 1970 | 1971 | 1976 | 1977 | 1978 |
|---|---|---|---|---|---|---|
| consumption in tons | 160 000 | 142 000 | 201 000 | 232 000 | 176 000 | 76 000 |
| NOTE: as an average, 1 Ton of chromite is equivalent to 300 Kilos of chromium. | | | | | | |

These data give an idea of ore importations.
However, the total consumption of chromium in Italy is higher as we import not only the ore (chromite) but also semifinished products (chromium-bearing steels, chromic acid, bichromate, ferroalloys).
In particular, the data supplied by ISTAT (National Institute of Statistic), Centro Inox, Assider and Siderleghe give the following informations on importations (+) or exportations (-):

| year | chromite | ferroalloys[1] containing chromium | stainless steel | chromic acid | bichromate |
|---|---|---|---|---|---|
| 1976 | + 232,000 | + 44 000 t | - 4100 t | + 500 T. | -7600 T |
| 1977 | + 176,000 | + 48 800 t | + 2700 t | + 130 T. | -7200 T |
| 1978 | + 76,000 | + 79 900 t | -32452 t | - 170 T | +10,400 T |

[1] Consisting mainly of " carburized ferro-chromium " (Cr = 60 - 65%) and " Charge Chrome " (Cr = 52 ÷ 58%) and to a much lower extent of "refined and superrefined ferro-chromium" (Cr = 75%), and "silicon-chromium" (Cr = 60%).

Italian Importations (+) or Exportations (-) of products containing chromium (Istat 1976 ÷ 1978)

| Year / Materials | 1976 | | | 1977 | | | 1978 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Imports (t) | Exports (t) | Balance (t) | Imports (t) | Exports (t) | Balance (t) | Imports (t) | Exports (t) | Balance (t) |
| Chromite ore | 234.912 | 2.961 | + 231.951 | 178.139 | 2.012 | +176.127 | 79.493 | 3.606 | + 75.887 |
| Chromium trioxide | 617 | 117 | + 500 | 520 | 389 | + 131 | 791 | 959 | - 168 |
| Another chromium oxides and hydroxides | 1.393 | 1.612 | - 219 | 1.054 | 647 | + 407 | 566 | 876 | - 310 |
| Chromium sulphates | 3.611 | 8.615 | - 5.004 | 2.731 | 8.146 | - 5.415 | 2.491 | 9.219 | - 6.728 |
| Chromium alum | 458 | 92 | + 366 | 351 | 105 | + 246 | 507 | 130 | + 377 |
| Lead and zinc chromate | 295 | 27 | + 268 | 3.391 | 55 | + 284 | 498 | 29 | + 469 |
| Another chromates | 408 | 1040 | - 632 | 269 | 1.077 | - 808 | 350 | 1.558 | - 1.208 |
| Sodium bichromate | 3.327 | 11.125 | - 7.798 | 3.772 | 11.017 | - 7.245 | 1.786 | 12.456 | - 10.670 |
| Potassium bichromate | 372 | 175 | + 197 | 82 | 88 | - 6 | 299 | 2 | + 297 |
| Another bi and per chromates | 35 | 32 | + 3 | 49 | 1 | + 48 | 27 | 74 | - 47 |
| Unrefined chromium and scraps | 155 | 6 | + 149 | 107 | 1 | + 106 | 197 | 86 | + 111 |
| Processed chromium | 23 | 8 | + 15 | 24 | 6 | + 18 | 9 | 4 | + 5 |
| TOTAL | 245.606 | 25.810 | +219.437 | 187.437 | 23.544 | +163.893 | 87.014 | 28.999 | + 58.015 |

As indicated in the table under para. 2), the iron metallurgical industry accounts for approximately 3/4 of the chromium used in Italy. Thus, it was deemed important to contact:

- Centro Inox, Milan (Center for the Study and Development of Stainless Steel)
- ASSIDER, Milan (Iron Metallurgy Industry Association)
- Siderleghe, Milan (Business firm dealing with the sale of ferroalloys)

Stainless steel production in Italy has been characterized by a continuous and constant increase whereby the production of ingots and tapped products for casting raised from 17,000 tons in 1955 to 450,000 tons in 1978. The figure is equivalent to 1.8 % of the total production of steel in Italy. Considering that in a stainless steel chrome is present approximately in the amount of 18.5%, this means that 80,000- 85,000tons/year of chromium are included in stainless steels.

The steels falling within the unified steels specified by UNI technical standards (National Italian Unification) and containing chromium are:

- alloy steels (chrome-manganese and chrome-vanadium)
- special alloy steels (silicon-chrome and silicon-chrome-molybdenum)
- steels for ball bearings (chromium and chrome-molybdenum)
- stainless steel and refractories (ferritic and martensitic; austenitic)
- for special uses (Ni-Cr; Cr-Mo; Ni-Cr-Mo; Cr-V; Si-Cr-Ni;

Cr-Si; etc.)

Another major consumption source of chromium in Italy is the tanning industry. The National Tanners Association, through its consultant Prof. Airoldi of the University of Turin, supplied us with data on chromium consumption in tannery.

Referring to 1975 data, we have:

| Type of hide | tons processed | specific consumption (gr.$Cr_2O_3$/kg. hide) | total consumption T. $Cr_2O_3$ | total consumption T. Cr |
|---|---|---|---|---|
| raw brined fresh cow or horse | 290,275 | 25 | 7712 | 5275 |
| raw dry or half-tanned sheep or goat | 33,297 | 50 | 3046 | 2083 |
| | | | TOTAL | 7358 |

As concerns the consumption of the refractory products industry, 25,000 tons of chromite were used in Italy in 1969. There is a strong trend to reduce the use of refractories containing chromium as the number of "Martin" furnaces for steel production (requiring chromium-base refractories) is decreasing.

According to ANIR (Associazione Nazionale Industrie Refrattari) estimates, the Italian production capacity of basic refractories (magnesitic and chromium-magnesitic) is 70,000 tons/year. The actual production was:

48,000 tons in 1975; 59,000 tons in 1976; 50,000 tons in 1977; 45,000 tons in 1978.

The foreign trade recorded in 1978 the following trend:

imports = 30,000 tons/year; exports = 32,400 tons/year

60% of the production is chromium-magnesite, 20% of which is represented by chromite; the latter's consumption in 1978 was 5,000 tons.

- As concerns the paints industry, the pigment consumption for paints containing chromium salts, - chromium yellow, molybdenum orange, chromium green - has been estimated in 1972 in 5500 tons. Chromium salts are also used in textile industries where are employed as base dye as well as in particular in after- chromating fixing solutions.

- As concerns the galvanic industry, the increasing use of plastic components in lieu of chrome-plated components, in the automobile field as well as in valves, involved no practical change in the consumption of chromic acid. In Piedmont, where a high number of manufacturers in this branch are located, the chromic acid consumption is at present approximately 700 tons/year.
  Furthermore, it is expected to replace the use of chromium salts with cobalt acetate.

## 4) Industries in Italy interested in chromium

The main industries using chromium are:

- iron metallurgical industry (stainless and special steels)
- refractory products
- tanning industry (chromium tanning)
- paints industry
- galvanic industry

Using ISTAT's statistical data (which refer to the last industrial census in 1971) and considering that a certain percentage only of the employees of these industries does a work connected with chromium handling (such percentage is based on an estimate made by us), we have calculated the number of employees whose work involves the handling of chromium.

| Industry | ISTAT classification | No. of employees | % of workers handling chromium | No. of workers handling chromium |
|---|---|---|---|---|
| Iron-metallurgy (cast iron, steel and ferro-alloy production) | 3.09.01 | 123 000 | 3% | 3700 |
| Ceramic, gres and refractory products | 3.12.09 | 77 500 | ~ 8% | ~ 6000 |
| Tanneries | 3.06.01 | 24 600 | ....... | ....... |
| Production & processing of non-ferrous metals | 3.09.06 | 41,200 | ....... | ......... |
| **Primary** chemical products production (chromium salts) | 3.13.02 | 73 000 | ........ | ......... |
| Metal surface and electro-galvanic treatments | 3.10.47 | 29 300 | ......... | ........ |
| Total employees of chromium processing industries | — | — | — | |

## 5) Substitution of Chromium

When we talk about substitution of chromium we not only mean the concept of substituting the metal with another, but also the concept of preventing the use of chromium or the recycle of processing or finished products waste in order to recover the chromium.

In the case of the metal under consideration, there is a double interest in recovering it from processing and finished products waste (when there are finally disposed of). In fact chromium, especially in the hexavalent form, is particularly toxic.

Consequently, many industries, like the galvanic industry, in order to prevent the costly purification treatments of liquid and sludge waste, prefer not use chrome-plating when this is not essential and substitute it with other materials.

The analysis supplies an evaluation of primary importance for our study, i.e. where chromium is or is not essential for a certain use. The table on the following page shows, for instance, the evaluation of Centro Inox on whether or not it is essential to use stainless steel containing chromium in certain industrial applications. In many instances, the analysis of this indispensability of the use of chromium will be the scope of the researches proposed to the European Economic Community, thus reference is made to paragraph 7).

## INDISPENSABILITY AND NON-INDISPENSABILITY OF STAINLESS STEEL IN CERTAIN INDUSTRIAL APPLICATIONS

| Type of industry | Application requiring stainless steel | Applications where stainless steel is not indispensable |
|---|---|---|
| Metal processing | - hardening boxes and similar | - pickling and cleaning<br>- painting boots |
| Chemical | - production plants of base chemical products<br>- petrochemical industry<br>- plastic material ind.<br>- fertilizers, explosives, paints, textiles, paper, tannery | |
| Power | - electric resistances<br>- nuclear plants<br>- steam turbines<br>- hypercritical boilers<br>- gas turbines | - power supply<br>- radio TV aerials and components<br>- industrial boilers<br>- burners<br>- solar collectors |
| Pharmaceutical | - base pharmaceutical substances,Galenicals etc. | |
| Cosmetics and parfumes | - production of essences, aromas and oils | |
| Textiles and dyeing | - weaving<br>- bleaching | |
| Food | - milk<br>- vegetable substances<br>- icecreams<br>- homogenized and baby food<br>- bread and pastry<br>- fruit<br>- animal fat and vegetable oils | - drinks (wine,beer, etc.)<br>- milking and butter processing<br>- meat processing<br>- fishing and fish processing<br>- sacchariferous<br>- fodders<br>- bread and pastry ovens |
| Transportation | - tail shafts, rudders<br>- airplane engines<br>- airplanes structures | - railway cars and street cars<br>- tankers<br>- containers |
| Building | | - outdoor metal components<br>- roof accessories<br>- bathroom and toilet access.<br>- barbers equipment |

| | | |
|---|---|---|
| Hospitals | - sterilization plants<br>- surgery rooms and instruments<br>- necroscopy | |
| Equipment for communities | - house electrical appliances<br>- laundry and drycleaning machines<br>- bars, snackrooms, canteen tables | - large kitchens<br>- laundries<br>- kitchen furnitures<br>- washbasins |
| Household articles | - cutlery | |
| Agriculture | - tobacco dessication and curing | - fertilizer, antipest and weed-killer |
| Ecologic plants | - waste incinorators<br>- furnace chains and carpets | - desalination and demineralizing<br>- water purification<br>- water collection |

Let's now see in detail the problems of substitution and recycle and recovery. The latters probably will be dealt with in a special study.

## 5.1) Substitution

The major replacements concern the field of chromium-steels, in particular of stainless steels.

There are several possibilities of replacement:

a) replacement of steels containing chromium with:

- Fe-Al alloys with carbide dispersion;
- Ti-Al compounds which seem to have good characteristics at high temperatures (gas turbine components); see also annex A

b) replacement of steels containing chromium with ceramic materials featuring:

- good abrasion resistance;
- good corrosion strenght;
- good oxidation resistance.

Generally, it concerns silicon carbides and silicon nitrides, aluminium oxide, different borides, etc.

Research is suggested in all three directions mentioned above from Fiat Research Center (see Annex B).

c) Another more radical substitution is the one adopted by some industries (for instance, automobile factories) where the chromium used for decorative chrome-plating has been substituted with plastic components.

Considering that in a medium displacement car (1100 cc) by substituting 560 dm$^2$ approximately of chrome-plated area with plastic material, 20 grams of Chromium are saved, and considering that in Europe

10 millions cars are manufactured every year, it would be possible to save in this way 800 tons approximately of Chromium (let's not forget that, as mentioned in para. 5.2 for 1 gram of deposited chromium, 3 grams of Chromium are lost, as the average yield of chromium electrodeposition is equivalent of 25%).

The substitution could be systematically extended to many other industrial and building applications where the chrome-plated and stainless steel structures have a decoration function. Substitution materials could be plastic materials, fibreglass-reinforced plastic, painted steel, etc.

Some Italian companies (Fiat Engineering, Fiat Research Center, Snia Viscosa, Breda Research Institute) are interested in the study and research on the matter.

d) As concerns the use of chromium salts in paints, it is possible to substitute chromium-base green and yellow pigments in 80% of the cases with other organic pigments already available on the market but so far little used because much more expensive than chromium salts. Textile industry should utilize better the use of chromium as the trend is to substitute the after-chromating fixing solutions, causing considerable wastes containing chromium, with dyes having already the correct amount of chromium salts required for fixing the colours.

e) It also seems possible for tanneries to reduce the use of chromium by introducing a new product called NEOCONC containing aluminium base polychloride, which should be suitable to substitute the use of $Cr_2O_3$ by 70%.

f) in the refractory industry, the substitution of chromium-bearing bricks with bricks containing magnesite only does not involve any problem from the technical point of view.

Chromite can be substituted with properly pure magnesite in order to maintain the same refractory quality.

In this connection, marine magnesite would be suitable as pit magnesite has considerable amounts of impurities which reduce the quality of the refractory.

The production cost of high quality magnesitic refractories is however almost twice that of good quality chromium-magnesite.

The high cost difference is the reason why chromium cannot be substituted.

No health-environmental work problem restricts the use of this material.

Thus, it is not envisaged to substitute chromite with magnesite until the high difference in cost will prevail.

EXAMPLES OF REFRACTORY MATERIAL COMPOSITION

| BASIC REFRACTORIES | Chemical analysis % | | | | | | | Volumetric weight Kg/cm$^3$ (1) |
|---|---|---|---|---|---|---|---|---|
| | MgO | $Cr_2O_3$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $B_2O_3$ | |
| Baked products<br>Quality super | | | | | | | | |
| M5 B - Magnesitic | 95,5-96,5 | — | 0,7-0,95 | 0,2-0,4 | 0,15-0,3 | 1,9-2,4 | 0,02-0,04 | 2,85-3,00 |
| MC 5 Chrome-magnesitic | 50-56 | 17-21 | 1,7-2,2 | 13-16 | 9,5-12 | 0,6-0,8 | — | 3,00-3,20 |
| MC 6 Chrome-magnesitic | 58-63 | 15-18 | 1,6-1,9 | 11-13 | 8-10 | 0,8-1,1 | — | 3,05-3,15 |
| MC 29 Chrome-magnesitic | 55-60 | 17-20,5 | 1,2-1,5 | 6-8 | 11-14 | 0,9-1,1 | — | 3,10-3,25 |
| CM 1 Chrome-magnesitic | 40-45 | 21-26 | 2,0-2,5 | 16-20 | 11,5-13,5 | 0,8-1,2 | — | 3,00-3,15 |
| Baked products<br>Special and Standard | | | | | | | | |
| M 2 magnesitic | 90-92 | — | 0,7-1,1 | 0,5-0,8 | 4,5-5,4 | 1,7-2,1 | — | 2,86-3,02 |
| M 3 magnesitic | 87-92 | — | 1,5-2,5 | 0,9-1,8 | 3,0-5,5 | 1,5-2,3 | — | 2,84-3,00 |
| MC 4 Chrome-magnesitic | 56-65 | 13-18 | 2,0-2,8 | 8-11 | 8,5-11,5 | 1,0-1,6 | — | 2,91-3,09 |
| CM 3 Chrome-magnesitic | 46-52 | 18-24 | 2,5-3,5 | 14-18 | 8,5-12,8 | 0,9-1,3 | — | 2,85-3,05 |

## 1 - Cr/Al ferritic stainless steel

By replacing in stainless steels a fraction of Chromium with Aluminium, it is possible to have a high resistance to oxidation in high temperature oxidative atmosphere for the formation of alumina oxidative films, the protection degree of which seems to depend on whether or not rare earth or Yttrium are added in the steel.

The proposed research aims to obtain a better knowledge of thermal oxidation mechanism in order to improve the behaviour of such steels to corrosion with respect to the cost of the added elements and to mechanical properties.

Other aspects of the study concern the behaviour in water solution at different degrees of attack (still to be defined especially with regard to traditional ferritic steels) and the influence of the metallurgical factors on other process characteristics (mechanical strength, ductility, weldability, etc.).

Considering that the chromium contents in a traditional ferritic stainless steel suitable for such uses can range from 18% to over 20%, with the new family of aluminium steel it is envisaged the possibility of replacing over 30% of chromium contents.

## 2 - Austenitic Mn/Al stainless steels

The partial and perhaps total substitution of Chromium in austenitic stainless steels is based on the aluminium action which added with large amounts of manganese could result in a steel with features hopefully similar to austenitic stainless steel.

Through compound variations in traditional austenitic stainless steels involving the partial or total replacement of Ni with Mn-Al and possibly of chromium, austenitic steels with mechanical properities deemed satisfactory and comparable to traditional austenitic steels are obtained. In addition to the requirement of a screening on the chemistry of such steels, there are no data about the ductility and toughness at lower temperatures than ambient temperature, as well as about the behaviour to dry and wet corrosion.

Scope of the research will be to set up, first in laboratory and then on a pilot plant, a manufacturing cycle for this type of steels, and to give a preliminary characterization of the properties of resistance to hot corrosion in oxidative atmosphere and in differently aggressive water solution.

## FIAT RESEARCH CENTRE

### Special ceramic materials as substitutes for chromium alloys

In the last few years special ceramic materials have taken on a particular role among the new materials which scientific research can profitably take into consideration to develop valuable alternatives to alloys containing high-quality or strategic elements such as Cr. and Ni. Special mention should be made of silicon nitride and carbide. In the last decade huge research efforts have been made in this area by both the industry and public research organizations, aiming at developing structural components resisting the high temperatures with the use of such materials.

The advantages of employing such ceramic materials as substitutes for high-quality metal alloys can be summarized as follows:

- the basic elements needed to make the finished products are cheap and abundantly available;
- although the ceramic industry is associated with high temperature processes, ceramic products can be regarded as relatively cheap in terms of energy requirements;
- the problems of environment pollution resulting from ceramic manufacturing processes are relatively small;
- recent experiments on the mechanical properties of ceramic materials have shown that also the traditional problems created by the material inherent brittleness can be at least partly overcome.

The main fields of application where metals can be successfully and efficiently replaced by ceramic materials are on the one hand high temperature processes (900 to 1400°C), and on the other components to be used in corrosive environments and where components are subjected to wear as well as to corrosion.

In either case ceramic materials can replace metal in applications where alloys with a variable content of chromium are currently being used. A successful solution in this direction can be expected, based on the properties of the materials developed to date, but further development is required as needed by each particular application.

To this end, a research program is being proposed with a view to developing and improving special silicon nitride and silicon carbide ceramic materials with processes consistent with industrial production procedures, for low and medium temperature applications, where such materials could be used instead of chromium alloys, leading to savings in costs.

The proposed research program should include three steps, namely:

- making an analysis of the situation in EEC countries in the mentioned field, as well as an estimate of the expected demand of such materials and a consequent evaluation of the amount of chromium that might be replaced;
- working our a detailed description of the properties of stainless steel and chromium-based superalloys and of special ceramic materials (especially those containing $Si_3N_4$ and SiC) and comparing the same in order to ascertain whether and to

what extent are substitutions possible;

- developing prototype components for the fields of greater interest and evaluating their performance.

The estimated period required by the research program described is expected to be three years, the first of which would be taken by the survey to collect information in all European countries, the other two mostly by experimental activity.

The estimated cost of the research will be in the area of 700 - 800 million Liras.

## Testimonial of the FIAT Research Centre

The activity of the FIAT Research Centre in the field of special ceramic materials can be summarized in six specific patents and the following publications:

"Devitrification phenomena of a pressureless sintered silicon nitride"
P.C. Martinengo, A. Giachello, P. Popper, A. Buri, F. Branda
presented at the Intern. Symp. of Hakone, Japan, 1978

"Sintering of silicon nitride in a powder bed"
A. Giachello, P.C. Martinengo, P. Popper, G. Tommasini
accepted by J. Mat. Science

"Fabrication and properties of a pressureless sintered silicon nitride base on $Y_2O_3$ as sintering aid"
A. Giachello, P.C. Martinengo, P. Popper, G. Tommasini
to be submitted to J. Am. Ceramic Soc.

"Densificazione del nitruro di silicio : alcune osservazioni sul ruolo dell'ossido di magnesio e di ittrio"
P.C. Martinengo, E. Mino
accepted by Ceramurgia

"Sinterizzazione di nitruro di silicio in 'Pack' : effetto dell'MgO"
A. Giachello, P.C. Martinengo, G. Tommasini
CRF Internal Report

"Post-sintering of reaction-bonded silicon nitride"
A. Giachello, P.Popper
to be presented at CIMTEC 4 - S. Vincent, Italy, 1979

"Sinterizzazione del reaction bonded $Si_3N_4$"
A. Giachello
CRF Internal Report

"Mechanical characterization of sintered $Si_3N_4$"
E. Campo, G. Ronchiato
to be presented at CIMTEC 4, S. Vincent, Italy 1979

"SPT relationships for sintered silicon nitride"
E. Campo, M. Castagna, S. Quaranta
to be presented at Science of Ceramics Meeting, Germany 1979

"Nitridation of silicon in air"
A. Giachello,
to be presented at Science of Ceramics Meeting, Germany, 1979

"Oxidation of sintered silicon nitride and its effect on the mechanical properties"
E. Campo, U. La Malfa
to be presented at Science of Ceramics, Germany 1979

"Sintered silicon nitride"
P.C. Martinengo, U. La Malfa
to be presented to AGARD Meeting, Germany, 1979

"Comportamento meccanico ad alta temperatura di un nitruro di silicio sinterizzato con additivi di $Y_2O_3$ e MgO"
E. Campo
CRF Internal Report

## TECHNICAL NOTE OF FIAT RESEARCH CENTER

### Cr SURFACE ALLOYING VIA LASER

(ECC Study)

Purpose of this research proposal is the use of power Laser for surface Cr alloying on technological steels not containing high amounts of this element. The ultimate aim of the research is to attain for the surfaces so treated properties comparable to chromium steels not using however high amounts of this element. Alloying tests have already been made on steels (1), (2), which showed how it is possible to obtain surface layers containing Cr of variable thickness from some ten of $\mu$m up to few millimeters. Corrosion, wear, fatigue tests are under way in order to ascertain the properties of the obtained surfaces.

The power laser employed in F.R.C. laboratories ($CO_2$ 15 KW, emitted radiation $\lambda = 10.6$ $\mu$m) enables to extend and generalize the alloying in general to many types of metal alloys.

Purpose of the research is therefore to carry out Cr alloying tests on low-alloyed steels in order to improve the knowledge about surface microstructure of the steels treated in such way, on microstructural stability, and on the relevant properties.

(1) D. Bacci - S. Tosto: AGARD Conference proceedings no. 256 (1978)
(2) D. Bacci - S. Tosto: COST 50 - Progress Report no. 1 (May, 1979)

## 5.2) Chromium recycle and recovery

Recycle in the classical sense (recovery of chromium from material containing it once the life of such material has come to an end) is very seldom possible.

It is instead possible to recover part of the chrome lost in the various processes. The following table gives an indication of process losses, calculated on the basis of consumption up to 1971:

| CHEMICAL USES | LOSS PERCENTAGE | CHROME CONSUMPTION TONS/YEAR IN 9 EUROPEAN MEMBERS | CHROME LOSS TONS/YEAR IN 9 EUROPEAN MEMBERS |
|---|---|---|---|
| ELECTROPLATING (CHROME-PLATING, ETC.) | 75% | 12,400 tons | 9,300 tons |
| HIDE TANNING | 25% | 7,500 tons | 1,800 tons |
| PAINTS | 5% | 14,300 tons | 750 tons |
| MISCELLANEOUS USES (CHEMICAL OXIDATIONS, PAINTINGS, CATALYSTS, PHYTOPHARMACY) | 10% | 14,300 tons | 1,500 tons |

The possible recovery is doubly important because:

- it saves strategic material;
- prevents or reduces a serious pollution source (chromium, especially in hexavalent form, is highly toxic).

There are two possibilities of recovery of galvanic industry losses, and these are being studied and investigated in Italy:

a) recovery of chromium from muds of galvanic water purification plants by hydrometallurgic processes (see Annex C);

b) recovery of chromium directly from galvanic industry baths by means of the combination of reverse osmosis and electrodialysis system (see Annex D) or other systems (demineralizing, evaporators, etc.).

Research in this field is suggested. If the recovery of half of the losses in the galvanic sector could be attained, a saving of 4 - 5,000 tons of chromium per year in Europe (versus a consumption of 380,000 tons/year) could be achieved.

Similar consideration applies to the tanning industry. We have in fact seen that this industry uses approximately 10,000 tons/year of $Cr_2O_3$ equivalent to 7000 tons/year approximately of Cr. In 1975, the loss percentage of chromium at discharge was 20% compared to the chromium used (i.e. approximately 2100 tons/year of $Cr_2O_3 \simeq$ 1400 tons/year of Cr). Since it is possible to recover, through proper techniques, such chromium losses, in whole or in part, if the waste is conveyed to a centralized treatment plant (1), it is assumed that bearing account of the tanning industry concentration in a restricted number of areas, and by equipping them with consortium treatment units for Cr waste and recovery, Cr loss can be reduced by half, i.e. down to 700 tons/year.

(1) For instance, in Santa Croce sull'Arno, a collection center for exhaust liquids and recovery of chromium contained in the same has been established.

## Fiat Studies on Centralized Waste Treatment Platform

A hydrometallurgical type of process has been perfected in the laboratory; this permits the recovery of copper and chromium from mud (thus making it possible to dispose easily of residual mud which is no longer toxic).
The experimented process is based on the dissolution of the two elements by means of diluted sulphuric acid, on the separation of the copper by means of cementation with iron powder, and on the precipitation of the chromium at controlled pH.

### a) Typing of muds

It should be noted that materials are not only present in the muds arriving from industrial water clarification systems but also from urban waters of highly industrialized areas.
At Collegno (province of Turin), for example, the following metals have been traced in the mud:

. Cr = 2,200 p.p.m. max; = 0,22%
. Cu = 1, 200 p.p.m. max; = 0,12%
. Fe = 10, 500 p.p.m. max; = 1,05%
. Pb = 240 p.p.m. max; = 0,02%
. Zn = 3, 200 p.p.m. max; = 0,32%

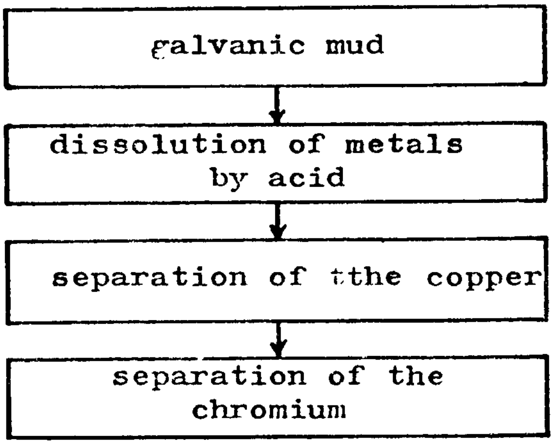
with a total metal content of more than 13, 000 p.p.m. = 1,30%

Later studies regarding the recovery of chromium and copper from muds have been carried out on a sample of mud from the galvanic industry containing:

| | | | | |
|---|---|---|---|---|
| . copper | equal to | 1.46% | as | CuO |
| . chromium | " " | 3.68% | " | $Cr_2O_3$ |
| . nickel | " " | 2.40% | " | NiO |
| . zinc | " " | 0.67% | " | ZnO |

b) <u>Preparation and laboratory testing of a process for recovering copper and chromium from industrial muds</u>

The technique adopted provided for the following flow scheme:



For the acid preparation of metals, chemical attacks with hydrochloric and sulphuric acid have been experimented: with the latter, less acid is consumed, it precipitates calcium as sulphate and a higher concentration of metals is obtained in the acid solution. The attack yield is 99.9%; residual mud,is sterile and can easily be disposed of without ecological problems.

The solution deriving from the acid attack has a pH of 1.5 and contains 14.3 g/l of Cu, 30.8 of Cr, 23.1 of Ni and 8. 8 of Zn.

The following techniques have been tested for recovering copper:

a) extraction with selective solvents;

b) electrolytic deposit;

c) separation by means of cementation with iron powder.

The final solution was adopted; the maximum yield temperature is about 60°C; the iron powder should be in quantities to 1, 2 times the copper present; a product is obtained which presents as a black, spongy agglomerate.

This copper cement can be sold as it comes to users as copper scrap or it can be refined thermally to obtain premium casting copper with a grading of more than 99%.

There are a number of possibilities for recovering chromium:

a) oxidation in an alkaline environment;

b) electrolytic oxidation in an acid environment;

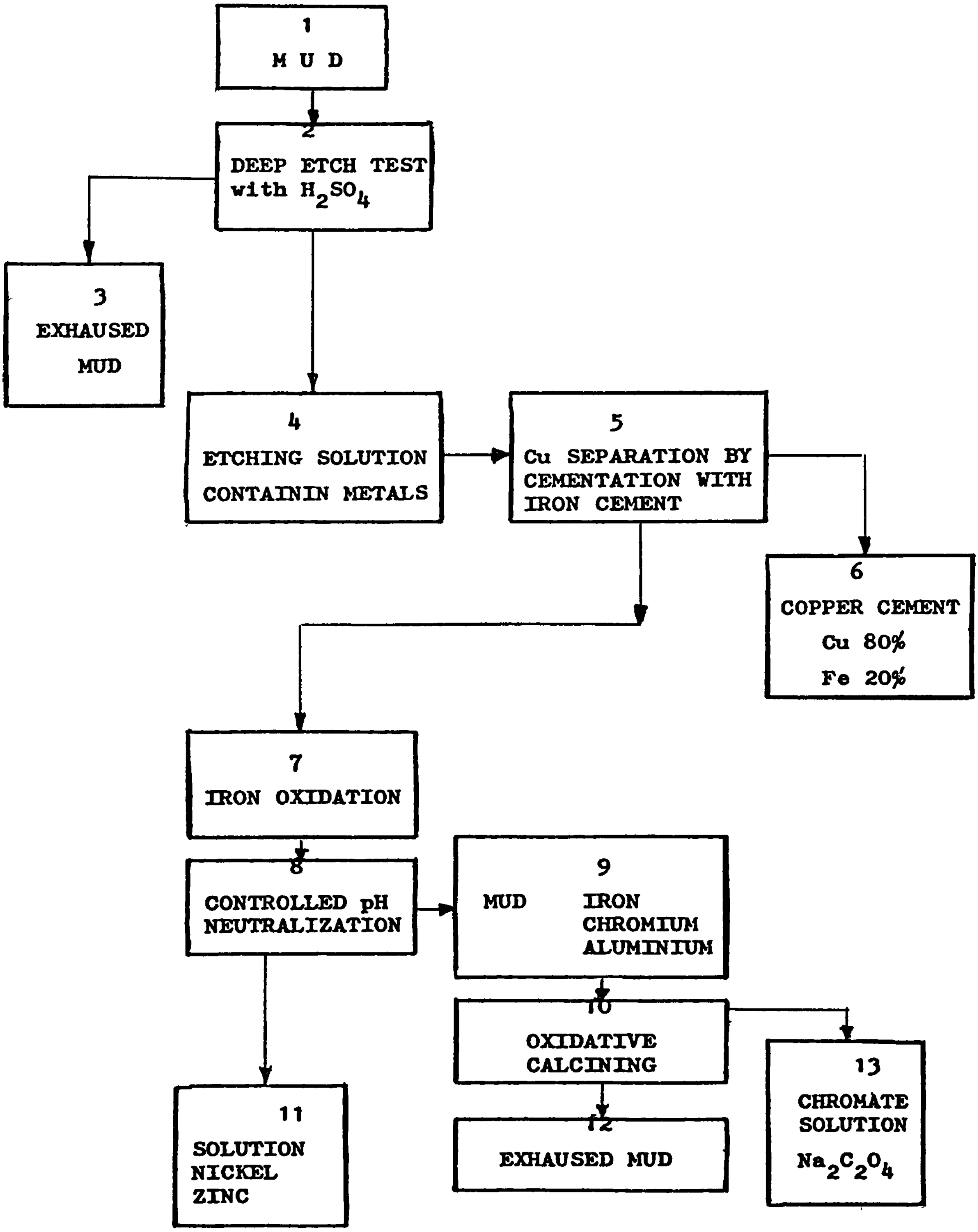
c) precipitation at controlled pH (to prevent co-precipitation of both nickel and zinc) and oxidative calcination.

The final technique proved to be the most convenient; pH is brought to 4, you precipitate and separate the solution containing all the zinc and nickel together with 10% chromium; the precipitate containing iron, chromium and alluminium is calcinated in an oxidative environment to obtain exhausted mud and a solution of sodium chromate.

The block diagram in figure 1 illustrates the recovery process.

We are currently looking into recovery techniques for metals when these are still in water solution. By combining reverse osmosis systems (as we are dealing with waters from the galvanic industry, a concentration of metal salts can be obtained) with electrodialysis systems (which allow the metals to be recovered from these concentrates) we hope to obtain direct recovery more economical than the one described here. Reverse osmosis systems could be installed within individual companies while the electrodialysis system could be installated in the "platform".

Figure 1 FLOW CHART



## PURIFICATION OF WATER FROM GALVANIC TREATMENTS BY COMPLETE RECYCLE OF EFFLUENTS

Electrodialysis is one of the techniques known todays, but not yet available for industrial application, enabling a "null disposal", i.e. it is possible to recover all the water used in washing operations which can be recycled as soon as it is free from foreign substances.

The salts properly concentrated by reverse osmosis processes are re-used in the same operation whence they originate.

Figure 1 shows a flow chart of purification and recycle of galvanic process effluents.

In actual fact, two products are obtained by means of electrodialysis process:

1. purified water
2. concentrated solution.

The purified water is recycled in washing operations. The concentrated solution is reversed in the electroplating bath.

The continuous treatment is performed according to the diagram in Figure 2.

An electrodialyzer is located between the treatment vessel and the first washing (likewise between the other two washingvessels). The electrolyte carried by each electrodialyzer is exactly equal to the carried electrolyte (in the opposite direction) consequent to the drag-out of the machined parts.

The discontinuous treatment system is attained by means of the diagram in Figure 3.

The solutions stocking tank consists of three separate sections. The cyclic functions of each section are the following:

- washing effluent collection,
- washing effluent purification,
- washing water supply.

Said functions periodically alternate during the process.

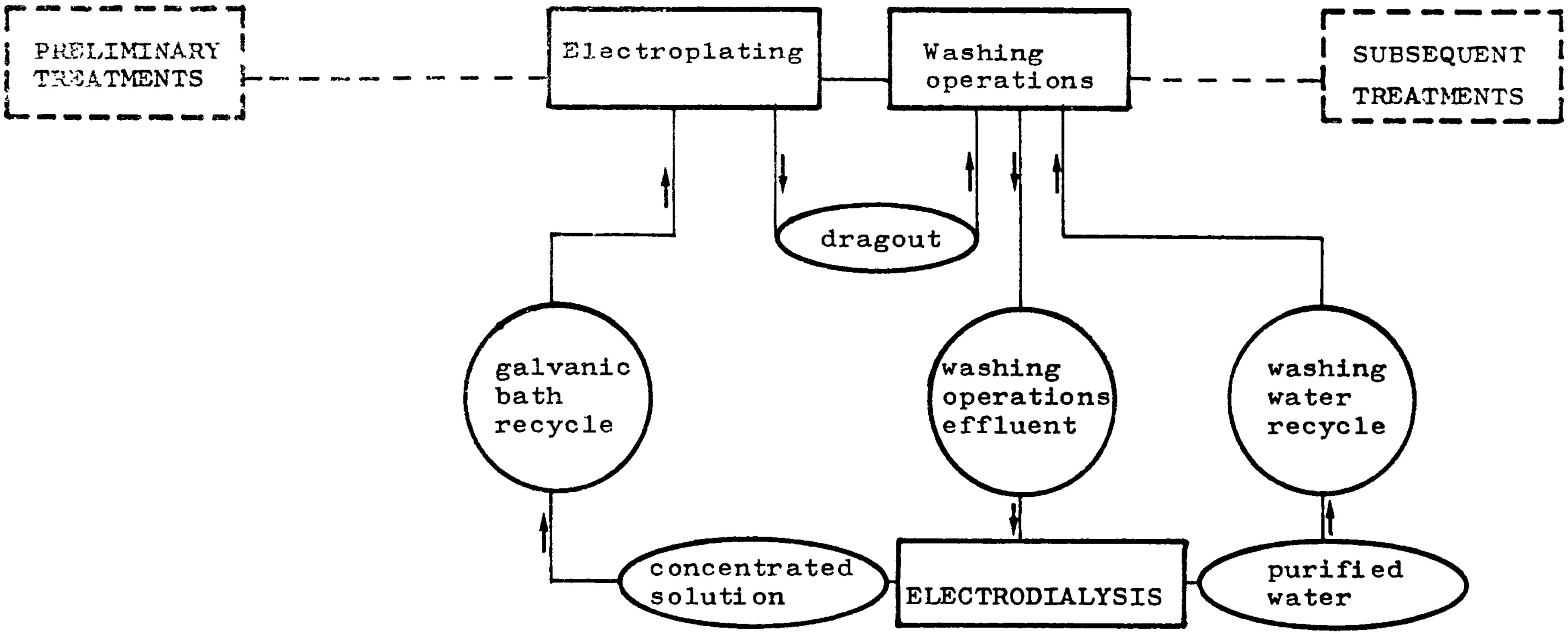


Figure 1 - Process flow chart

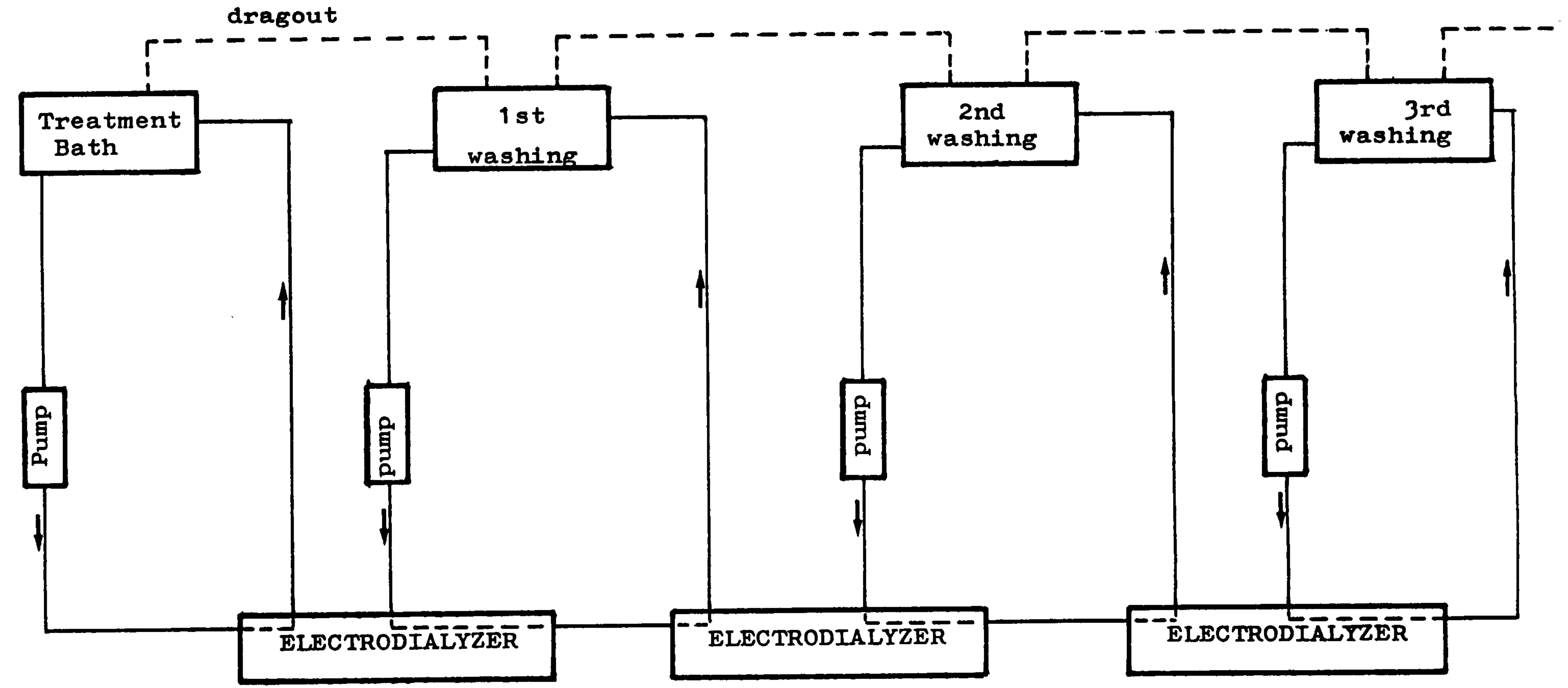


Figure 2 - Practical diagram of continuous treatment of washing waters.

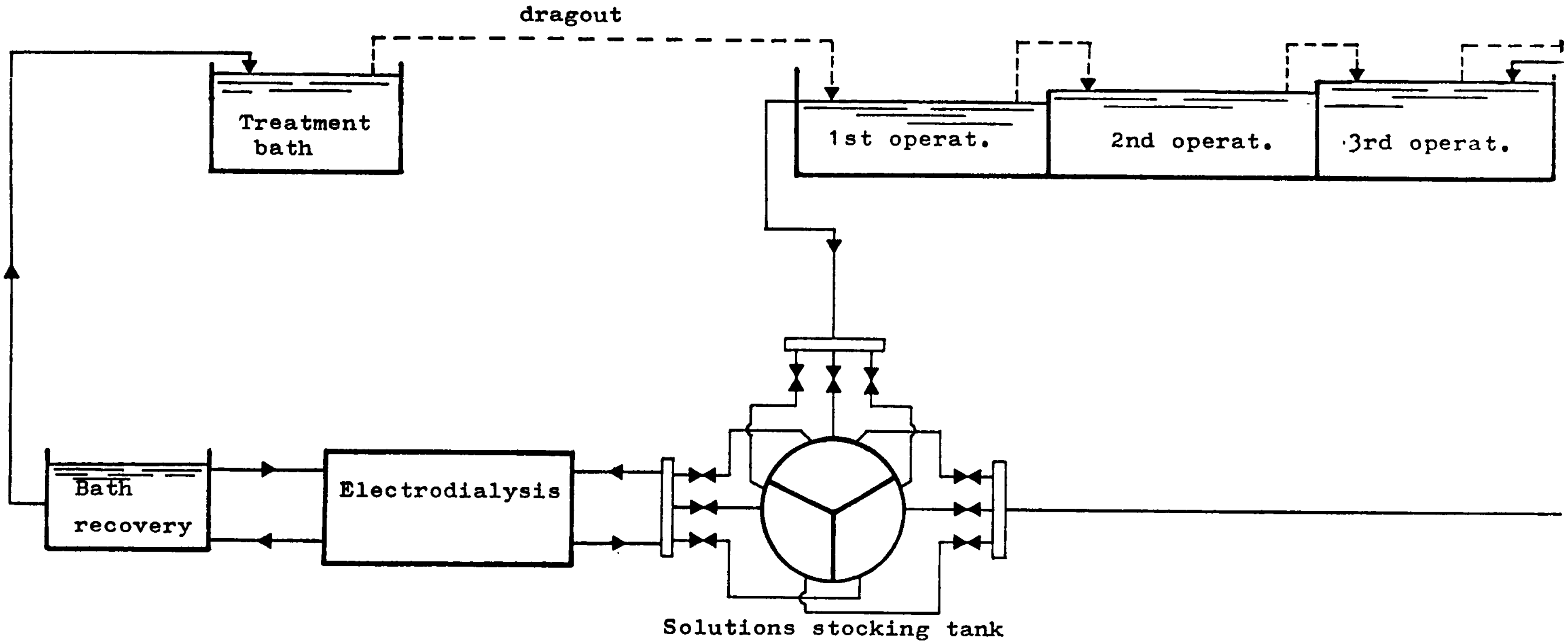


Figure 3 - Practical diagram of washing water treatment discountinuous process

## 6) CRITICALITY

- In 1972, the following was exchanged in the world:
  - 4.3 million tons of ore (equivalent to 60% of world production)
  - 0.7 million tons of ferrochromium (equivalent to 35% of world production)

Italy, always in 1972, imported:

- 215,000 tons of ore
- 84,000 tons of ferrochromium

The ore (Turkish ore) costed in June, 1976 $ 130 - 140/ton, while the metal (98 - 99% pure) costed $ 6,150/ton in December, 1977 in New York.
The price increase trend (in constant terms of the currency value) is estimated in 1 - 3%/year.

- The criticality is represented not so much by the restriction of the world ore reserves (it is estimated they will last another 70 - 75 years) as by the fact that 2/3 of the production is concentrated in only 4 politically sensitive areas (USSR, South Africa, Rhodesia, Albania).

- If we consider that:
  - 3/4 of chromium is used to produce stainless and alloy steels of primary importance for the European manufacturing industry and the use of which is constantly increasing,
  - another 2[illegible]% is used to produce refractory material used especially for siderurgical furnace linings

we see that chromium availability is vital for European iron metallurgical industry.

- Another industry, too, widely developed in Italy for instance, depends on chromium. It is the hide tanning industry, where the substitution of chromium would involve the production of tanned products with quite different characteristics (change of contraction temperature, softness, etc.).
- The establishment of a possible cartel among some producing countries or the interruption of ore exportations by some of the more politically unstable producing countries, would automatically cause a crisis in the supplies and consequent unavoidable price increase of the end product containing chromium (and thus crisis for their production). Furthermore, this would mean a considerable burden for the balance of payments (200,000 tons of ore at approximately $60+100/ton and 80,000 tons of ferroalloys at $ 750+800/ton mean approximately $70+80 millions/year of importations for Italy alone).

## 7) CONCLUSION AND RECOMMENDATIONS

The conclusions of this analysis on the use of chromium can be summarized as follows:

a) a crisis in the supply of chromium would involve directly approximately employees of siderurgical, refractory, tanning, galvanic and paint industry, and indirectly 1.6 million workers approximately in the mechanical and plant construction fields, large users of stainless and alloy steels.

b) the distribution of chromium consumption for the different end products is as follows:

| | |
|---|---|
| - stainless and alloy steels | 80% |
| - refractories | 2% |
| - paints | 2% |
| - galvanic | 1,5% |
| - tannery | 11% |
| - other uses (superalloys, chemical products) | 3,5% |

c) Recoveries are possible in galvanic industry (where 3/4 of chromium is lost) and in tanning industry (1/5 lost); the total loss of chromium is approximately 3.5%. The development of recycle systems reducing such losses to about one half would enable to save 1.5 ÷ 2% of the chromium used.

d) a large saving is however possible only in the stainless steel field, large consumer of chromium. Consequently, the major efforts must be made in the partial substitution of chromium with other materials (aluminium, manganese) for the production of stainless steels. If it were possible to reduce by 1/3 the consumption of chromium in stainless steels, the saving would be equivalent to 25 ÷ 30% of the chromium used.

e) another source of large saving is the substitution of chrome-plated or stainless steel components,with a mainly aesthetic function, with plastic components in the manufacture of transportation means as well as in the building industry.

This analysis leads to the proposed research work:

- study of stainless steels containing less chromium (see section 5.1 - Annex A): value of the proposed research 700 million Lira.
- study of special ceramic materials as substitutes for chromium alloys: value of proposed research approximately 800 million Lira (see section 5.1 - Annex B)
- recycle of chromium contained in galvanic baths and recovery of chromium from mud (see section 5.2 - Annexes C and D): value of proposed research approximately 500 million Lira
- study of recycle centers of tanning waste with recovery of chromium (see section 5.2): value of research approximately 200 million Lira
- study and research on substitution of chrome-plated or stainless steel components with other components of equivalent function, manufactured of plastic material; fibreglass reinforced resin and painted steel (see section 5.1); value of studies and researches million Lira.

## 8) LIST OF CONTACTED PERSONS, COMPANIES AND ORGANIZATIONS

The following persons or organizations in Italy interested in the use of chromium have been contacted:

- Prof. S.W. Venceslai - Ministero delle Partecipazioni Statali, Roma;
- Centro Ricerche Fiat - Orbassano (Torino);
- Centro Sperimentale Metallurgico - CSM, Roma;
- Centro Inox - Milano;
- Assider - Milano;
- Soc. Siderleghe - Milano;
- Prof. Airoldi - Università di Torino (per Associazione Conciari).
- Istituto Donegani - Novara
- Teksid - Torino

COMMISSION OF THE EUROPEAN COMMUNITIES
(Directorate General XII - Research, Science and Education)

APPENDIX B to WSL Report

# CHROMIUM SUBSTITUTION STUDY

Report for the Netherlands

by

M.J. Reidt, J. Van Garderen and C. deGroot

1) A study about electrolytic chrome plating with $3^+$ chromium *

2) Corrosion resistant heavy chrome plating **

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*) TNO report nr. 79 M/36/08844/REI/BGN
**) TNO report nr. 79 M/36/08846/REI/BGN

# A STUDY ABOUT ELECTROLYTIC CHROME PLATING WITH 3+ CHROMIUM

## Introduction

For chrome plating, decorative chrome plating and hard chrome plating generally chrome solutions which are compound of chromium acid ($CrO_3$) are applied with a low content of 3+ chromium and sulfate, and/or silicofluoride applied as a cathalyst.
Since 1925 these electrolytes are used very often, also by development's work of Liebreich in Germany and Fink e.a. in the United States, which has lead to a stable process. However, these chromium acid electrolytes have in practice some disadvantages, such as a low cathode efficiency, a poor covering power and a limited throwing power.
Sensitivity for current interruption and tending to patch forming if the chromium is deposited on bright nickel.
For chrome plating a product quite well, auxiliary anodes are very often necessary. Chromic acid as an electrolyte is poisoned and environmental pollutioned and gives for the electro plater reason for attack of the nasal septum and for chromic ulcers at fingers and hands.
For as far as it is cancer causing is not known yet, but an investigation has started.
It is to be expected that some difficulties with respect to the future will occur.

For the practice holds that in any case the chrome solutions will be easy in composition and furthermore will be unexpensive as well as it will be less complicated in use.
By limited admissibility of 6+ chromium in effuent water it is necessary to reduce till 3+ chromium and after it can be deposited by neutralisation of the solution and filtration till slutch forming is possible.
This treatment is complicated and expensive as well as with respect to investments and treatment costs.

In 1854 already you can find literature information concerning 3+ chrome solutions, but till 1933 there is a lack of new information.
After 1933 there are some publications and patents such as those of Kasper and of Lloyd of the United States Bureau of Mines.
The extraction and processing of chromium by means of electrolytes was first found in 1957 by Union Carbide and promoted on big scale.
In 1950 a research was started on 3+ chromium electrolytes. Investigators in the United States, Japan and Great Britain have published a lot about this matter, and several patents are the result.
Complexing agents were very often used, such as ureum, carboxyla acids, ammonium salts, haligenides and organic solvents such as dimethylformamide etc.

From these developed electrolytes, they have all more or less disadvantages, applying for decorative chrom plating in the electro plating world with respect to dependability; a property that 6+ chrome solution misses.
The solution is in practice extremely cheap, for chromic acid is the cheapest pure chromic compound that ever exists and the accompanying sulpher acid as a cathalyst/impurity is a part of the electrolyte.
However, in the future chromic acid is limited in the for the electro plating world useful quality, in connection with scarcity and political developments in the chromic ore owing countries.
New, similar and better solutions are considered to be necessary.
The 6+ conventional chrome solutions are less sensitive for disturbing strange metals, such as Fe, Cu, Zn and Al. The elimination of chloride is often a very expensive matter for the concentration is mostly maximal 50 mg/l.
The 3+ solution is more sensitive for metal impurities and in this respect it is to be compared with an organic bright Ni-solution. The disturbing metals can continue with a lower current density or be eliminated by precipitation and filtration.
Current interruption does not bear 6+ chrome solutions, for this results in white or grey spots in the deposits. For 3+ chrome solutions this has not any effect. Principally, 3+ chrome solutions would possess more advantages but practice shows the opposite.

## I.1. Electrolyte composition of new solutions

Although chromium of 3+ solutions with chromic alum succesfully can be won electrolytically, many effects for developping a useful and reliable solution have lead to an extremely applicability of which in many cases it gives reason for severe critisism.

Studying the international developed 3+, decorative chrome solutions, that generally seems to work exellently, but in practice gives less good results, three trends are to be distinguished:

a) solutions on water base with many dissolved salts,
b) solutions on base of organic liquids,
c) complexed solutions.

### I.1.2. Composition CrII, CrIII and CrVI

From CrII solutions it was sometimes possible to get bright deposits in an N2 atmosphere (P1). Generally it was stated that the deposition of a CrIII solution first then became possible after a big part (± 50%) was transposed into CrII. Also in present patents publications the 3+ chrome solutions are subjected some time to electrolyse before the right qualities are obtained.
During the electrolyse dependently of the accompanying elements, forming of CrVI on the anode takes place, while also air of CrII oxydises to CrIII. Every 3+ chrome solution measure taking care of CrVI reduces till CrIII again (reduction means, organic compounds or the impurification of the electrolyte by CrVI has to prevent like seperate anodic-cathodic cells by diaphragmas. The concentration on CrIII is important lower than the one for CrVI solutions, namely ± 40 g/l is a much occurring concentration.

### I.1.3. Accompanying anion

Efforts to deposite Cr out of 3+ chrome solutions are performed with the chromium III salts: chloride, sulfate, nitrate, jodide, fluoride, perchlorate, fluoborate, acetate, formate, oxalate and glyolate. Out of nitrate solutions no chromium was obtained.

Also the simple salt solutions of complexed acatates, oxalates and tartrates did not give succesful deposits.

Dependent of additions for bright deposits are mentioned with:

Chloride - S5, B2, Y1, C2 W2
Sulfate - P1, F4, B4, K3, G4, D7
Fluoborate - K3, D7
Oxalate - M8
Glycolate - B14
Formicate - L10

An unsoluble anode the anion $Cl_2$ or CrVI is formed independently; the chloride that exists on the anode can be made innocuous at once by adding ammonium salts or other $NH_3$ compounds. Applying sulfates a diaphragma of the CrVI with methanol or sulfite must be reduced. Reducing anions are able to let this reaction happen. Recent developments where preferably is worked without diaphragma, indicate in the direction that chloride as an accompanying anion without diaphragma gets good results (D7). Using carbon-anodes in presence of $NH_4$ ions, sulfate ions proved strong attack of the anode. Also here with an addition of chloride the situation improved.

(Albright and Wilson see the Dutch paten application 7202360-1972)

### I.1.4. Conducting salts

See table anion II and cation II.

In all written receipts the anion of the conducting salt is almost the same as in the accompanying anion of the CrIII.

If the chromium salt is used as an organic acid compound, one makes a choice for an anorganic acid rest. For example for glycolate solutions the chloride ion (B14). The cation can be the Na, K or $NH_4$ and if KCl will be chosen as a conducting salt, the deposit will be white like silver (F1).

The ammonium has as an advantage that this reacts with $Cl_2$ and the anode till chloride and nitrogen.

In common, it will be stated that by adding of conducting salts the cathode efficiency will improve.

### I.1.5. Anorganic additions

Boric acid is an addition that as well as in chloride as in sulfate conditions has a favourable action. In the recent developed DMF solution (dimethylformamide) boric acid is added.

In fluoride containing solutions it must be accepted that the boron for a part is present as fluoborate and of which has also a posssitive effect on the outlook.

With presence of glycerol (D7) the borium is present as boroglycerine. Some metals are mentioned as a positive addition namely; Fe, Co, Mg in sulfate solutions and Al and Mg in chloride solutions. In the DMF solution metal ions work disturbing. The acceptable concentrations for Fe, Ni and Zn are < 15 ppm. From the above mentioned it can be concluded that the 3+ chrome solution is more sensitive for the metallic impurities than the 6+ chrome solutions.

### I.1.6. Organic additions

In literature only a few additions are mentioned. In common it can be stated that they must have one or more of the following properties:

a) reducing propertie with regard to CrVI

A large number of compounds react with CrVI in an acid environment+ Applications take place with methanol, glycerine, tartaric acid, glycol, acid, oxale acid, ureum etc.

b) reducing properties with regard to $Cl_2$

For these $NH_2$ connections are mentioned such as ureum, formamide, acetamide, etc.

c) complexing properties with regard to CrIII

Compounds such as hydroxid acids, armino acids, dicarbon acids are considered for this.

d) wetting agents

From patent literature it follows that cation active wetting agents improve the coating.

e) organic solvents

In literature organic solvents are mentioned only limited. The deposition in high current density areas can be improved with betrahydrothiophene-dioxyde- dimethylformide, N methylpyrodlidon, demthylsulfon, ethers and thio-ethers.

The low current density area is enlarged by compounds such as phenol, cresol, xylenol, resorcinol, ureum, melanirna, acrylamide, analine etc.

## II. Preparation of the 3+ chrome solutions

For obtaining a good deposition of a 3+ chrome solution, many failures are a result of the way of preparation of the chrome solution. Being dependent of the chrome complex (violet of green form) and the eventual solution the preparation of the chrome complex is dependent on $CrO_3$ and on a maximum temperature of ± 40 °C.

After aging the greem modification is transformed into violet and chromium can also be deposited at a lower current density.

By this fact the working temperature for certain 3+ chrome solutions is limited.

### II.1. The way of preparation of $Cr_2(SO_4)_3$

The preparation of $Cr_2(SO_4)_3$ from $CrO_3$ (D7) is executed with $CH_3OH$ and $H_2SO_4$. The $CrO_3$ is solved in the half of the needed water and concentrated supher acid. A solution of 1 part methanol and 2 parts water are added in small parts; ruddered strongly and cooled such that the reaction temperature will remain below 30 °C.

For a complete redection 102% of the theoretical quantity is as follows:

$$2CrO_3 + CH_3OH + 3H_2SO_4 \longrightarrow Cr(SO_4)_3 + CO_2 + 5H_2O$$

After finishing the reaction, at room temperature the solution ia aged within 10 hours and in the absence of $CrO_3$ is tested with $H_2SO_4$ at which phenylanthranil acid is added.

### II.2. The way of preparation of Cr glycolate

The preparation of Cr glycolate according to Dupont patents 3706636-43 happens as follows:

In a barrel is brought together 0.8 mol Cr, 1.8 mol glycol acid (70%) and 0.5 mol HCl (37.3) and the reaction temperature increases as a result of this till 75 °C.

Subsequently, it is heated till 88 $^{o}$C after which all the chromium will solve after ± 4 hours. Subsequently, during 2 hours and heated under 107 $^{o}$C back cooling, the reaction melting is thinned till 40 g/l Cr while 15 g g/l KCl and 63 g/l $H_3BO_3$ is added and after which the pH is brought on 2.94 with an alkaline solution.

## III. Anodes

### I.1.1. Chrome anodes

The use of chrome anodes without diaphragma is known from literature (C2 and S5). To prevent passivity phenomena, combinations of for example alternating current or direct current are chosen.

The solutions by using Cr anodes are chloride solutions with a high cathode efficiency of 85-95% (A4) and with a composition of:

| | | |
|---|---|---|
| $CrCl_3$ | 260 g/l | |
| $NH_4Cl$ | 50 g/l | |
| $H_3BO_3$ | 10 - 20 g/l | temperature > 20 $^{o}$C |
| $NH_4SCN$ | 40 g/l | Dk 8 - 12 A/dm$^2$ |

### I.1.2. Graphite anodes

Graphite anodes with a diaphragma are applied by numerous experiments to deposite chromium from 3+ solutions. Also the more recent solutions on base of $CrCl_3$ and dimethylformide are equipped with graphite anodes and later even without diaphragmas. The Dutch application nr. 720364 of Albright and Wilson deals with the matter of the carbon anodes in the 3+ chrome electrolyte. In this patent application it is stated that during absence of Cl-ions a certsin attack of the carbon takes place and that little carbon particles are even found in the deposit. By addition of Cl-ions on the anode, chloride is formed, however, instead of chromic acid. This $Cl_2$ is taken away by reaction of $NH_4$ ions or on organic N compound under forming of Cl-ions and $N_2$. In presence of ureum $CO_2$ and $N_2$ are developed, which should be more favourable for the carbon anode.

From descriptions of the LVCD solution of Dupont also in absence of ammonium salts and dimethylformide there will be no forming of 6+ chrome.

### III.1.3. Other unsoluble anodes

In sulfate solutions used as electrolyte Pb is often used as an anode resulting in an improvement of forming of 6+ chromium. Pb is not recommanded as anodic material (D7) and they preferre Fe-Si alloy. Presence of Fe in sulfate electrolytes should be more favourable. Also Ag is very often used for investigation.

## IV. Solution maintainance

Information from literature is very scarce. Generally by using metallic anodes or by frequent completion of metal salts, the composition can be maintained.

With electrolytrode forming of chromium from chromic alum one works with unsolble anodes (Ag-Pb-1-99) and diaphragmas. The chromium is added by means of chromic alum, for ammonium sulfate is realisable in both compartments because the preparation of chromium- and ironammonium sulfate by recirculation of the anolite and catholite as well as with a constant composition.
By constant circulation of the catholite through the diaphragma the development of 6+ chromium is prevented. The anolite is treated with $SO_2$ to reduce 6+ chromium before a mixture of chromium and ironammonium sulfate is added.
At experiments of the MDF solution (BNF) for maintaining the pH and chromium alloy, the addition of chromium hydroxyde is chosen as being the solution.
Worth mentioning is that maintainance is very well possible, for the drag losses and the deposited chromium are keptunder control by the basic chromium chloride in the solution.

Copper, nickel and iron impurities are removed under continuation with room temperature and 1 $A/dm^2$ while Zn is 6 $A/dm^2$ at 40 $^oC$.

Solution composition BNF

| | |
|---|---|
| $CrCl_3$ 6H2O | - 213 g/l |
| $NH_4Cl$ | - 26 g/l |
| NaCl | - 36 g/l |
| boric acid | - 2 g/l |
| dimethylformamide | - 400 g/l |

Working conditions

| | |
|---|---|
| temperature | 25 ± 5 °C |
| pH | 1.1 - 1.3 |
| current density | 10 - 15 A/$dm^2$ |
| voltage | 10 - 15 V |

Y.E. Bright mentioned with his description of the LVCD solution (Dupont de Nemours) that as a result of the fact that the solution is started with a so called organic-anorganic complex that is a compound of chrome, a prime organic element and an hologene; this solution also can be used for solution maintainance.

COMPOSITION LVCD

| component | recommandation | limits |
|---|---|---|
| organic-anorganic complex | 266 ml/l | 220-320 ml/l |
| chromium (metal) | 40 g/l | 33- 48 g/l |
| conducting salts | 244 g/l | 202-248 g/l |
| secondary organic element | 10 ml/l | 8 -12 mol/l |
| acid neutralisation addition | pH 3.1 | pH 2.85 - 3.2 |

WORKING CONDITIONS

| component | recommandation | limits |
|---|---|---|
| temperature | 26 °C | 22 - 40 °C |
| cathodic current density | 7.5 A/$dm^2$ | till 22 A/$dm^2$ |
| deposition time | 1 - 3 min. | ½ - 10 min. |
| temperature | 30 °C | 28 - 30 °C |
| pH | 3.1 | 2.85 - 3.25 |

By applying thin layers, the brightness is dependent from the roughness of the under layer. The LVCP solution indicates that the reflectivity is 40% while the decorative chromium VI is above 70%.
The deposition is micro-porous till 0.25 µm and micro-cracked from 0.25 up till 1.25 µm.
When it is higher than 1.25 µm it is useless and therefore uncapable for hard chromium applications.

The corrosion resistance in favour of the micro-porous or micro-cracked character of the deposition is in combination with bright nickel on steel the same compared with 6+ chromium solutions that deliver a micro-porous or micro-cracked chromium and better than normal chromium.

## VI. General conclusions

The reliability of till now designed 3+ chrome solutions is surely too low.
A demand is that a weekly and simple analyse must be sufficient to guarantee a constant quality of the electrolyte and deposit.
The 6+ chrome solutions is cheap in composition and maintainance. The higher usebility of the 6+ chrome solution especially for hard chrome gives possibilities for using or evaporation in connection with effluent water treatment.
Chromic acid is the cheapest form in which this metal in natural form is available on the market;
chromium as a metal is in unnatural from also a cheap raw material that can become scarce for political reasons.
The 3+ chrome solution has mostly a lower action temperature (25 °C) which blocked reducing and closed loop systems.
The hardness and wear resistance of 3+ chrome is lower than of 6+ chrome, which is a hamper for the competition.

The selection for making a program of investigation for which only a few solutions are considered, looks as follows:

a) the chrome solution on base of chromium. chromium chloride and dimethylformide
b) the chrome solution on base of chromium glycolate
c) a chrome solution on base of chromium sulfate, ammonium sulfate and boric acid

d) combinations of a, b and/or c.

## VII. Practical future possibilities for 3+ chromium

### 1. Barrel-chrome

A great advantage of for example Dupont and also BNF solution is the bright range area that can be obtained and which is important for barrel chroming. Current interruption does not have any influence on the outlook of the deposit.

Applying barrel chroming on base of 6+ chromium and adding fluoride is very limited because profiled articles cannot be treated.

### 2. Chromium with tampon

Also chrome-brush plating is a possibility of the 3+ chrome solution although this is limited among others till the printing industry.

### 3. Decorative chrome with plating jigs

The 6+ chrome solution is a reliable solution in favour of action security in operation, process costs. This can cause big problems in favour of the availability of chrome connections and the immense effluent water problem. If the present and many obstacles of the 3+ chrome solutions could be solved, than many perspectives are open for still chrome vat plating on jigs.

### 4. Hard chrome plating

The on 3+ chrome based solutions have the disadvantage that only thin layers can be deposited.

It is not to be expected that the possibilities for thicker chrome layers will enlarge by investigation. It is better to exclude applications for hard chrome, for the time being, and in this field to search how the corrosion- and chemical resistance can be enlarged by means of a combinated system of chrome layers.

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## CREST CHROMIUM SUBSTITUTION STUDY

## Corrosion Resistant Heavy Chrome Plating

### Introduction

In this report is in the title the conventional term "hard chrome plating" deliberately avoided. The methods of obtaining corrosion resistant heavy chrome deposits are closely related to the now generally practilly know processes for hard chrome plating. In some aspects there is a considerable difference of the chrome deposits in respect to the mechanical properties and in appearance.
There are two mutually independent methods of producing corrosion resistant chromium deposits:

a) so called "double chrome plating" and the single-stage corrosion resistant heavy chrome;

b) the so called "cold chrome plating".

Crack free, highly micro cracked and micro porous chrome can be obtained under certain working conditions and is effected by the choise of the chrome-electrolyte. Precise control over these conditions is then a "must".
According to the electrochemical potential series, chromium is very much baser than iron.
Theoretically it must follow that chromium should protect steel very well but on account of the passivation phenomena and the associated positive change of potential it is essential for corrosion resistant chrome deposits on steel that these should be free of pores and cracks.

There is no difficulty in obtaining thin crack- and pore free bright chrome but as soon as the thickness of the deposit is brought up pores and cracks will be produced.

I. Double hard chrome plating

It is known that raising the plating temperature of a sulphuric and acid chrome electrolyte diminishes the tendency to form cracks but increases the development of pores in thin layers. With the decrease in formation of cracks an improvement in corrosion resistance is reached.

To achieve the same effect as that by raising the plating temperature, the content of foreign acids can be lowered and the current density simultaneously reduced. These conditions produce crack- and pore free deposits which are corrosion resistant but not sufficiently hard enough for wear.

In general chrome deposits which are between "milky grey and bright milky" in appearance can be stated that the resistance to wear is poor. At the same time in such a case the current efficiency and consequently the deposition is so low that the plating times are unacceptable in practice.

A method which can satisfy users and producers of chrome deposit that is better resistant to corrosion and wear may be the following:

a) a deposit which is highly resistant to corrosion with a thickness of about 50 microns;

b) a hard wear resistant layer on top of a).

These requirements are satisfied by so called "Double hard chrome plating".

In contrast with the double chrome plating in the decorative sector the first layer deposited by this treatment remains crack free.

It has repeatedly been claimed and now can be taken as an accepted fact that crack free, though in some cases very brittle, chrome can be deposited from a sulfuric acid electrolyte at less than 30 °C. A proces for depositions relatively soft layers operates with a chromic acid content of 200 - 400 g/l $CrO_3$ and a $SO_4$ concentration of 0,45 - 0,75 % g/l at 20 - 35 °C with a current density of 60 - 120 $A/dm^2$. The 7 - 20 microns thickness produced by this treatment is supposed to be more corrosion resistant than 20 - 30 µm of the conventional chrome plate. Deposits from solutions with a higher sulphuric acid content are mostly described as brittle. The appearance of the chrome is namely in this case dull and grey.

Double hard chrome plating consists of a two stage treatment with a deposit of 5 - 8 µm from a so called "hot chromium solution" and is pore- and crack free. The temperature of the hot chrome solution is about 70 °C and the current density of 25 - 30 $A/dm^2$ with a plating time of about 30 minutes. With a relatively low concentration of sulphuric acid this solution contains ± 300 g/l $CrO_3$ and a CrIII content of less than 1 g/l $Cr_2O_3$.
Next the articles are rinsed in hot water of about 65 °C and are then chrome plated in a special hard chrome solution with a current density of 50 - 60 $A/dm^2$ and a temperature of 55 - 65 °C. The chrome deposit should have over 300 cracks per cm and for a freshly made up electrolyte to max. 1000 cracks per cm. To avoid violent cooling and the consequent risk for forming cracks, rinsing afterwards is carried out at steadily falling temperatures.

## II. Cold chrome plating

Cold chrome plating operates at temperatures of 25 ÷ 28 °C and current densities of 30 ÷ 40 A/dm$^2$ and delivers a disarranged fine grained chrome structure. Violent cooling or rapid heating of the chrome plated parts must be avoided.

The cold chrome electrolyte may contain 400 g/l $CrO_3$ and 4 g/l $H_sSO_4$ or/and a special catalyst. Limitations to the thickness of the deposit has to be accepted.

Deposits from solutions with a high sulphuric acid content are mostly brittle. The appearance of the plate is then dull and grey.

The cold chrome plating proces which can produce crack- and pore free deposits is never used as a first step in double chrome plating.

Unfortunately it is not yet possible to deposit micro cracked hard chrome working conditions.

## III. Surface finish before plating

One of the most important demands for depositing corrosion resistant chrome plate is that the base metal should have a satisfactory surface finish. That means that the surface of the base material must be free of cracks, pores, cavities, grooves, scratches and rust spots.

This quality can be achieved by adequate pretreatment of removal of rust, oxides, grease, dirt and oil <u>but is not enough</u>.

Roughness depths of $Rt < 1$ µm and $Ra < 0{,}5$ µm should be the target.

Mechanical treatments can cause small folds and overlaps which are pressed into the base material. These folds can be opened by electric etching and can lead to poor corrosion resistance.

## IV. Applications

Double chrome treatment was first put to use in wear- and corrosion resistant chrome plating in hydraulic systems for mining purposes; for construction machinery, to calender rolls and so on.

The life time of a hard chrome system can be enlarged for 50% - 100% or more if we know the facts and datas to produce the right type of deposit.

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