

# COMMISSION OF THE EUROPEAN COMMUNITIES

COM(83) 189 final

Brussels, 14 April 1983

Proposal for a  
COUNCIL DIRECTIVE

on procedures for harmonizing the programmes  
for the reduction and eventual elimination of  
pollution caused by waste from the titanium  
dioxide industry

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(submitted to the Council by the Commission)

COM(83) 189 final

## 1.- INTRODUCTION

On 20 February 1978 the Council took a further step towards implementing the Action Programme of the European Communities on the Environment of 20 December 1973 by adopting Directive 78/176/EEC on waste from the titanium dioxide industry (referred to as the "basic Directive"), the declared aim of which is "the prevention and progressive reduction, with a view to its elimination, of pollution caused by waste from the titanium dioxide industry".

The Directive stipulated appropriate means to achieve that end, and in particular that the competent authority of the Member State in whose territory the waste was produced was to issue prior authorizations for all discharges and that programmes for the progressive reduction and ultimate elimination of this form of pollution were to be drawn up.

Article 9 in particular called on the Member States to draw up programmes for the progressive reduction of pollution caused by waste from titanium dioxide plant and to send them to the Commission by 1 July 1980 at the latest.

The programmes were to cover all existing  $TiO_2$  works and to set general targets for the reduction in the level of pollution by liquid, solid and gaseous wastes to be achieved by 1 July 1987 at the latest; they were also to contain intermediate objectives. Finally, the programmes were to include information on the state of the environment concerned, on the measures taken to reduce pollution and on the methods used to treat the waste arising directly from the manufacturing process.

## 2.- RECEIPT OF THE PROGRAMMES

2.1.- As required by Article 9(3) of the basic Directive, the Commission duly received the Member States' reduction programmes, in the following order :

- 3 July 1980 and 7 January 1981 - United Kingdom
- 22 July 1980 - Federal Republic of Germany
- 21 November 1980 - France
- 30 November 1980 - Italy
- 7 January 1981 - Netherlands
- 15 October 1981 - Belgium.

2.2.- After a preliminary analysis of the programmes, the Commission came to the conclusion that the data disclosed by the Member States were inadequate to allow it to send the Council appropriate proposals for the harmonization of the national programmes concerning the reduction and eventual elimination of this form of pollution and to improve the conditions of competition in the titanium dioxide industry by the prescribed deadline.

They were not identical, or even comparable; nor did they give exhaustive replies to Article 9(2). All this made it impossible for the Commission to reach a general assessment of all the programmes.

### 3.- CALL FOR FURTHER DETAILS

3.1.- To help it fulfil its obligations, on 22 May and 30 November 1981 the Commission asked the Member States for further details, adding that its representatives were prepared to visit the competent authorities or, if desired, the works managers concerned.

More specifically, the Commission asked for the following further details in connection with the sulphate process :

- (i) the volume of copperas (1) and other solid wastes currently stored;
- (ii) the practical steps taken to treat discharges to the atmosphere at all stages of production at certain plants;
- (iii) the 1981-87 timetable for achieving the general targets for the reduction of pollution;
- (iv) the total tonnage of acid effluent discharged, its composition and the dumping frequency and conditions;
- (v) the total budget earmarked for the series of studies leading up to the introduction of the anti-pollution measures, plus details of the total budget for the construction of land-based tips where the wastes could be totally or partially neutralized;
- (vi) an estimate of the annual cost of implementing the pollution reduction programmes;
- (vii) the investment costs and technical features of the land-based copperas storage facilities together with details of the tonnage dumped at sea.

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(1) "Copperas" is the common name for ferrous sulphate in the heptahydrate form ( $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ ), a by-product of the reduction and subsequent crystallization of the solution following digestion of the ilmenite.

3.2.- Some of the replies which the Commission received still failed to provide full answers.

4.- PROPOSAL FOR A COUNCIL DIRECTIVE AMENDING DIRECTIVE 78/176/EEC OF 20 FEBRUARY 1978 ON WASTE FROM THE TITANIUM DIOXIDE INDUSTRY, AND IN PARTICULAR THE TIME LIMIT FOR SUBMISSION OF THE PROGRAMMES FOR THE REDUCTION OF POLLUTION

As pointed out in Section 2.2, the Commission departments were forced to ask the Member States for further details.

To allow itself time to analyse the national programmes in the light of that new information and then to make the appropriate proposals to the Council, the Commission asked for the time limit to be extended to 30 October 1982. A proposal to that effect was put to the Council on 20 July 1982. (1). Council Directive 83/29/EEC of 24 January 1983 duly extended the deadline to 15 March 1983. (2).

5.- COMMENTS ON TITANIUM DIOXIDE

This Section simply gives a brief description of the various  $TiO_2$  production processes, of the composition of the wastes which they produce and of the most common waste disposal methods employed. Fuller details are set out in the communications concerning the proposals for a Council Directive on (a) methods for the surveillance and monitoring of the environments affected by wastes from the titanium dioxide industry (COM(80)831 final, 17 December 1980) and (b) waste from the titanium dioxide industry (COM(75)339 final, 14 July 1975).

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(1) O.J. C 196, 30 July 1982, p. 6.

(2) O.J. L 32, 3 February 1983, p. 28.

## 5.1.- Manufacturing processes

The manufacture of titanium dioxide pigments entails the production of extremely pure  $TiO_2$  from an ore in which it is mixed with other substances.

There are only two industrial-scale processes, both of them involving digestion of all the ore followed by selective extraction of the titanium compound and, finally, conversion of that intermediate compound into titanium dioxide.

They are known as the "sulphate" and "chloride" processes respectively.

The sulphate process is by far the most common in Europe.

### a) Sulphate process

This is the process which generates most of the waste. Different starting ores can be used in it, for example :

- (i) Ilmenite - which contains approximately 55 % titanium dioxide, 40 % iron oxide and 5 % other oxides, the exact percentage depending on the origin of the ore - is digested with  $H_2SO_4$ .

First the ore is ground and mixed with  $H_2SO_4$  in digestion towers, where it is converted into sulphates such as titanyl sulphate, ferrous sulphate and ferric sulphate, subsidiary sulphates and so forth. The resultant cake is dissolved in acid liquors and then reduced, by adding metallic iron to obtain ferrous sulphate. The residue from the digestion process is washed and stored on land, leaving solid waste.

- (ii) After crystallization and dewatering to remove some of the heptahydrate ferrous sulphate, i.e.  $FeSO_4 \cdot 7H_2O$ , (solids known as "copperas" are obtained) the liquor is concentrated and hydrolyzed to obtain titanium hydroxide. This gel is separated from the acidic mother liquors (20-23 %  $H_2SO_4$ ) by filtration, leaving strong acid effluent.

Following thorough washing of the gel - a process which leaves weak acid effluent - calcination in rotary kilns at between 900 and 1 100 °C produces crude  $TiO_2$ , which must then be ground to obtain the basic pigment. Some times, this pigment is subjected to further surface treatment to develop the product's properties as a pigment to the full.

- (iii) Canadian slag, on the other hand, with its high concentration of  $TiO_2$  (between 70 and 72 %) and only 12 % iron oxides and various other impurities, results in significantly less iron and acid waste being discharged. Compared with ilmenite, approximately one-third less acid effluent is produced for each tonne of end product and one-eighth the amount of iron is discharged. No copperas is formed from slag.

The basic manufacturing process is the same.

In conclusion :

The liquid effluents and hence the acid discharges can be traced to a number of sources, notably :

- (i) the mother liquors left after the separation phase which follows on from the hydrolyzation to obtain titanium hydroxide (these contain between 20 % and 23 % free sulphuric acid and are therefore designated "strong acid effluent").
- (ii) The weak solutions left after the washing phase which follows on from the separation stage. These contain between 5 % and 7 % sulphuric acid and are therefore designated "weak acid effluent";
- (iii) other wash waters.

The following solid wastes are produced :

- (i) crystalline ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) - copperas - if the starting ore is ilmenite. Once the reduction solutions have been crystallized, this waste can be separated out by centrifuge for re-use.

(ii) insoluble unreacted ore which is generally washed and dried to remove most of its acidity and then stored.

(iii) Finally, there are the gaseous wastes or discharges to the atmosphere, which can take various forms, e.g. :

- $SO_x$  discharges containing  $SO_2$  and  $SO_3$ , which are emitted from the digestion towers and calcination kilns;
- dust, whether black (from grinding the ore) or white (from grinding the pigment and milling the end product).

The combined annual production capacity of all the  $TiO_2$  plants using this process is approximately 730.000 tonnes.

#### b) Chloride process

The traditional starting ore for the chloride process is natural rutile, a scarce ore very rich in  $TiO_2$  (approximately 96 %), or, alternatively concentrates generally obtained from ilmenite or synthetic rutile.

The process involves chlorination of all the ore, with the resultant titanium tetrachloride then being mechanically separated from the other chlorides and distilled. Finally, titanium dioxide is obtained by oxidation of the titanium tetrachloride.

This process produces relatively little waste. However, it is not suitable for ilmenite-based concentrates, for which an iron-removal stage is required - a method of pretreatment which creates much the same problems as the waste from the sulphate process.

As a rough estimate, the combined annual production capacity of all the  $TiO_2$  plants using the chloride process is approximately 140 000 tonnes.



### c) Conclusions

The precise composition, of the wastes depends on the starting ores used, the manufacturing process and the treatment which the solid, liquid and gaseous wastes undergo at each stage of production.

The sulphate process is the one most commonly used in the 16 units currently operating in the Community, with their combined annual production capacity of approximately 870 000 tonnes. Leaving aside gaseous emissions, four categories of waste are produced - insoluble unreacted ore, copperas or ferrous sulphate, strong acid effluent and weak acid effluent.

### 5.2.- Principal waste disposal methods

Normally the sea provides the dumping grounds for discharges of wastes from the titanium dioxide industry, though under certain circumstances the wastes are dumped in fresh water, stored on land or injected into deep-lying strata.

#### Dumping at sea

There are three main methods of discharging effluent into the sea, namely :

- (i) by pipeline from the coast;
- (ii) from special dumpships out at sea;
- (iii) by submersion of neutralized sludges beneath the euphotic zone.

The pipeline-method normally entails diluting the effluent before discharge and selecting a discharge point from which it can disperse rapidly. The acid is neutralized by dilution and by the buffering effect of the sea.

Dumping at sea, on the other hand, requires specially-equipped tanker vessels, which release the acid direct into their wake, thus ensuring rapid dilution and sinking of the effluent to greater depths.

A sudden fall in the pH value of the receiving water is the most striking short-term chemical effect of dumping waste from the  $TiO_2$  industry from sea-going vessels. Due account has been taken of this in the provisions of the Oslo Convention relating to waste from the titanium dioxide industry, which stipulate that the pH of the receiving waters must return to a level of 6 within six minutes of the discharge.

The final method involves dumping the sludges produced during neutralization of the mother liquors (i.e. of the acid wastes) in deep water out at sea. Special devices discharge the sludges well below the euphotic zone.(1)

#### Discharges into surface waters

This method is used for acidic solutions which have been neutralized beforehand. The solid by-products are stored with the copperas.

#### Storage on land

"Tipping" is normally reserved for the small fraction of insoluble waste, i.e. substances which were not dissolved by the  $H_2SO_4$  when the ore was digested.

In addition, acid effluent can be neutralized with calcium carbonate and slaked lime ( $Ca(OH)_2$ ) and then stored on land. The same applies to copperas.

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(1) Euphotic zone: zone in which photosynthesis by chlorophyll takes place.

### Injection into underground strata

This method involves neutralizing the acid solutions and then pumping them deep into the ground. None of the industrial-scale  $TiO_2$  plants in the Community uses this method.

### Recycling

In some plants the acid solutions are recovered, reconcentrated and recycled. In others, copperas is roasted and converted to  $H_2SO_4$ , sulphur being added.

Other potential outlets for the waste have also been considered, e.g. treatment of the waters to obtain drinking water, iron oxide pigments, flux for the cement industry and weed killer. However, all these application would dispose of only limited amounts of copperas.

## 6.- PROGRAMMES SUBMITTED BY THE MEMBER STATES

Without infringing Article 13(3) of the Directive on waste from the titanium dioxide industry, below the Commission sets out a brief description of the pollution reduction programmes put forward by the Community's  $TiO_2$  producing countries. Full account has been taken of the further information requested and of the replies subsequently received.

## 6.1.- FRANCE

France submitted a relatively exhaustive document, starting with a general survey of all the  $TiO_2$  plants in France and then proceeding to outline each production unit individually, the current situation there and, finally, the programmes devised to reduce the level of pollution which they produce, under the following heads : strong acid effluent, weak acid effluent, discharges to the atmosphere and solid waste.

### 6.1.1.- Thann et Mulhouse works at Thann

(annual production capacity : 24 000 t)

The main line of business at this works is anatase titanium dioxide, which is produced by the sulphate process from (since 1979) a mixture of ilmenite and Canadian slags containing around 70 %  $TiO_2$ . This has already cut down the volume of acid required and the copperas residues produced.

Strong acid effluent : The strong acids are neutralized completely before discharge. The clear supernatant liquid is discharged into the River Thur, while the neutralized sludges are stored on land.

Weak acid effluent : Weak acids are discharged into the river once they have been neutralized. One improvement planned is to construct a homogenization pond and also a holding pond which would normally be empty but could accommodate excess effluent in the event of inadvertent pollution.

Discharges to the atmosphere - improvement plans : There are plans to fit all the digestion towers with gas scrubbing systems (only a few have them at present). Studies are now under way to eliminate  $SO_2$  discharges from the calcination kilns, which are already fitted with scrubbing systems to remove the dust and  $SO_3$ . All the crushers and grinders had been fitted with dust recovery systems by January 1982.

Solid waste : At the Thann works an impermeable barrier was constructed in the aquifer in 1980 to prevent contamination of the groundwater by iron salts such as copperas, while in 1982 improvements are to be made to the treatment system to protect the groundwater during the high-water season. Finally, the studies on re-use of the iron salts are to continue and in particular the programme for roasting with a view to regeneration of  $H_2SO_4$  and calcination to produce iron oxide pigment.

#### 6.1.2.- Thann et Mulhouse works at Le Havre

(Annual production capacity : 80.000 t)

Rutile titanium dioxide is produced at Le Havre by the sulphate process, with ilmenite and another higher-grade ore as the feed-stock. Recovery of some of the ferrous sulphate initially discharged and the decision to switch to higher-grade ore have now put an end to ferrous discharges from the plant. Nevertheless storage facilities for 600.000 tonnes of ferrous sulphate are available, just in case there is ever a shortage of high-grade ore.

Strong acid effluent : As a provisional solution, the acid liquors are being discharged into the Seine estuary by pipeline. In 1982, calculations based on a mathematical model of the dispersal patterns for a solution with a higher density than the receiving medium suggested that a diffuser and a 300 m pipeline were needed; both are now under construction. Two raised holding tanks will supply the diffuser with effluent whenever the current is strong enough to ensure optimum dilution; i.e. a pH higher than 5.5 within 50 m of the outlet at all times.

Weak acid effluent : One improvement planned is to construct a drainage system to keep the cooling water separate from the other liquors, which will be channelled to the existing purification plant, where settling ponds are to be added.

Discharges to the atmosphere : Thann et Mulhouse has studied the prospects of extending the technology of its most modern digestion towers to all the digestion towers at the Le Havre works. The off-gases from the calcination kilns are cleaned by a scrubbing system followed by highly efficient wet electrostatic precipitators.

The company has also considered replacement of the three conventional  $H_2SO_4$  production units by a new double-catalysis  $H_2SO_4$  unit.

Solid waste : The solid waste from  $TiO_2$  production takes the form of the sludges which are separated from the digestion liquors. Some 250 to 300 kg is produced for every tonne of  $TiO_2$ . Once the sludges have been washed and neutralized, they are stored.

#### 6.1.3.- Tioxide works at Calais

(Annual production capacity : 65 000 t)

Since 1967 Canadian slag - a high-grade ore containing 70 % titanium dioxide - has been used as the feedstock at the Tioxide works, which employs the sulphate process. As a result, no ferrous salts (copperas) are discharged into the aquatic environment, whereas around 200 000 tonnes a year would be dumped if ilmenite were treated.

Strong acid effluent : The strong acid wastes are discharged direct into the coastal waters from a 1 300 m pipeline (measured from the dune banks), with an outlet 5 m below sea level, or between 10 m and 15 m below the surface. Effluent is pumped into the sea discontinuously, with two storage ponds to hold the liquor between discharge periods.

Weak acid effluent : These too are discharged direct into the coastal waters. Consideration is now being given to a number of ways of improving the effectiveness of the treatment methods suitable for this class of waste.

Discharges into the atmosphere : Gas emissions from the digestion towers at the Calais works will be neutralized completely from 1982 onwards. The possibilities for improving the efficiency of the scrubbers are to be assessed by 1983 and, depending on the findings, work can be expected to go ahead between 1984 and 1986. Finally, the total dust emissions from the works are to be reduced from the current  $150 \text{ mg/m}^3$  stp to  $50 \text{ mg/m}^3$  stp in 1982.

Solid waste : Non-reacted waste which is insoluble in  $\text{H}_2\text{SO}_4$  is the only form of solid waste discharged. It is decanted, washed and dried and then stored in the purpose-built spoil tips on site. After two or three years, this waste is recovered for use as filling materials.

a) The French authorities pointed out that neutralization is the only viable solution to the liquid effluent problem at the current stage of research.

However, they could not contemplate imposing it unless it were adopted at Community level and applied to all  $\text{TiO}_2$  plants.

b) As an alternative, the tests on reconcentration and, perhaps, re-use of the acid wastes are continuing. Once a more satisfactory solution than neutralization has been devised, the Le Havre and Calais works will be expected to apply it to their effluents within five years.

c) The French authorities also sent cost estimates for each project concerning technical improvements intended to bring about a progressive reduction in pollution. The public authorities will draw up the timetable for implementation of these projects case by case, in the light of each plant's plans for investment in anti-pollution devices.

## 6.2.- ITALY

The Italian authorities submitted a programme covering the plants in operation when they received notification of the Council Directive. Spinetta Marengo's works at Alessandria in Piedmont, which came into operation in 1955, closed down in August 1979. There are no plans to reopen it before 1 July 1987.

### Scarlino works operated by SIBIT

(Annual production capacity : 50.000 t/an)

When the works first started operation in 1972, Norwegian or Australian ilmenite was the starting ore. By March 1980, progressive introduction of slag with a  $TiO_2$  content of 85 % had put an end to the production of copperas (ferrous sulphate).

Strong acid effluent : The effluents (free sulphuric acid) are neutralized with calcium carbonate and shipped for discharge at sea from vessels fitted to release the liquor approximately 100 m below the surface, i.e. beneath the euphotic zone, and at bottom depths ranging from 1 000 m to 1 700 m.

Weak acid effluent : Following neutralization and decantation in specially designed tanks, the supernatant liquor is discharged into the aquatic environment. There are plans to improve and rationalize the purification plant.

By 1983 the measures proposed would significantly reduce the volume of sludge produced, by reducing the volume of  $H_2SO_4$ , improving the neutralization process and selecting the best-suited neutralization agents.

Discharges to the atmosphere : All the polluted gases produced at the various stages of the production cycle are given appropriate treatment before emission from the works, for example by passing them through dust collectors, scrubbing towers with subsequent neutralization and decantation, or sleeve filters. There were plans to set up, by 1981, a regional network consisting of 13 monitoring stations to keep a watch on the gaseous emissions and to record the  $SO_2$ , suspended particulates and  $NO_2$  emissions. On the ground,



a local CO<sub>2</sub> monitoring network automatically cuts off emissions from the neutralization unit in the event of excessive accumulations.

Solid waste : The non-reacted ore is washed, neutralized and stored on land in pits lined with an impermeable material, subject to a study of the hydrological features of the soil.

Replacement of ilmenite by higher-grade ore put an end to the production of copperas (ferrous sulphate) and hence to the progressive encroachment on the land. All the necessary steps have been taken to ensure that the existing ferrous sulphate tips are watertight, that the pits are impermeable and that there is no seepage. The same applies to the sludges produced during neutralization of the strong and weak acids (these sludges are occasionally stored on land).

The Italian authorities gave no details of the cost of the pollution reduction programmes.

### 6.3.- NETHERLANDS

The Dutch authorities sent the Commission their pollution control programme for TDF Tiofine, whose Rotterdam works - which employs the sulphate process - has an annual production capacity of 35.000 t. It ties in with a Decree issued under the law on the pollution of surface waters (WVO) in the light of Council Directive 78/176/EEC on waste from the titanium dioxide industry.

The Decree authorizes Tiofine to discharge effluent into the Nieuwe Waterweg. However, the permit includes a clause that Tiofine must stop discharging acid wastes within two years of the date on which the authorization takes effect.

The underlying idea is that the company must take a number of internal measures to stop the acid discharges, either by treating the acid effluents which contain free  $H_2SO_4$  or by switching from the  $H_2SO_4$  process to another. If, at least six months before the deadline expires, Tiofine produces evidence that the deadline cannot be met, but that a four-year limit is needed instead, the two-year deadline could be extended by one year, after which a further one-year extension might be considered. If, however, before the two-year deadline expires it becomes clear that it will not be possible to end the discharges within either two or even four years, consideration could be given to discharges of the mother liquors into the North Sea for a limited period. Under Dutch law discharges into the North Sea require a dispensation issued in accordance with the Law on the pollution of seawater (WVZ).

The authorization covers the following aspects :

- (i) the points of discharge;
- (ii) the types of discharge permitted at each point (e.g. cooling water, rinsing water, etc.);
- (iii) the maximum permissible annual discharges of sulphuric acid, iron salts and solid matter and the dilution conditions to be met each day;
- (iv) the conditions under which the cooling water and other effluents from the plant is to be discharged (i.e. volume, temperature and chemicals);
- (v) the conditions to be met before the authorization can be extended.

Tiofine has appealed against the Decree, which cannot take effect until the appeal court gives its ruling. In view of this situation the pollution control programme linked with the authorization cannot yet enter into force either.

#### 6.4.- FEDERAL REPUBLIC OF GERMANY

The Federal Government's communication concerning its programme for the reduction of pollution caused by waste from the  $TiO_2$  industry is divided into two parts - one setting out the general objectives for a reduction in the level of pollution, the other giving an account of the specific measures taken to reduce pollution from the individual production plants.

##### 1.- General objectives

The overall objective of the programme is to bring about a progressive reduction in the level of pollution caused by liquid, solid and gaseous wastes from  $TiO_2$  plants. Germany feels that the 1987 target must not be considered the ultimate. More stringent requirements will be imposed with the advance of scientific knowledge concerning (a) the impact of the emissions and (b) the technologies available for reducing and eventually eliminating them. The communication explicitly states that the programme definitely does not intend to transfer pollution from one area of the environment to another.

- Strong acid effluent : At present some 1.72 million tonnes of acid waste is discharged into the high seas each year; approximately 430 000 tonnes per year, or 20 % of the total volume arising, is recovered by means of reconcentration and recycled. However, it is not economic to recover more at the moment because of the high cost of energy and the saturation of the market for the reconcentrated acids.
- Weak acid effluent : Weak acid effluent is dumped in the inland waterways; since 1 January 1981 a levy proportional to the load imposed on the environment has been charged for such dumping. A reduction in the level of these discharges, or at least in the amount of pollution they cause, is expected.

- Solid waste

- a) At present 240 000 t of copperas ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) - in other words, 44 % of the total amount produced - is recovered and reused each year. Some 70 000 t per year is dumped at specially authorized tips. The rest is discharged into the sea along with the acid waste. The target is to put an end to dumping of copperas at sea by 1 July 1987 at the latest. In 1981 some 110 000 tonnes was expected to be discharged. The German authorities hope that the discharges will stop altogether in 1984, three years earlier than planned.

A programme of studies on the development and utilization of copperas is planned.

- b) The insoluble non-reacted ore must all be stored on land by 1 July 1987 at the latest; at the moment some is still dumped at sea.

2.- Measures taken in the individual production plants

The German authorities also sent details of the 1987 targets for each plant, based on their 1975 waste production figures.

2.1.- Bayer AG production unit I at Krefeld-Uerdingen

(Annual production capacity, including 20 000 tonnes from unit II which employs the chloride process : 95 000 t)

Production unit I employs the sulphate process.

- Weak acid effluent

The measures taken include more efficient recovery of the acid to reduce the volume of acid discharges and recycling of the waste waters within the manufacturing process; together, these will reduce the acid load in the effluent by 32 % and the iron content by 47%.

- Discharges to the atmosphere

In 1981 a gas scrubber was added to clean the off-gases from roasting and digestion. This should reduce the pollutant load by approximately 75 %, i.e. 300 tonnes per year.

2.2.- Kronos Titan production unit I at Leverkusen

Annual production capacity, including 30 000 tonnes from Unit II (the chloride process unit) : 85 000, of which up to 70 000 t may be derived from the sulphate process and up to 35 000 t from the chloride process, though the aggregate total must not exceed 85 000 t under any circumstances.

- Weak acid effluent

Special electrodes and improved spraying in the scrubbing towers will reduce the SO<sub>2</sub> load in the gaseous emissions by 12 %, or by 752 tonnes per year.

2.3.- Kronos Titan production unit III at Norderham

(Annual production capacity (sulphate process) : 60 000 t)

- Weak acid effluent

By taking the same measures as at the previous unit, it should be possible to reduce the sulphur load of the weak acid effluents by 41 % and their iron content by 24 %.

- Discharges to the atmosphere

There are plans to reduce the SO<sub>2</sub> load in the off-gases by 4 % (current level : 610 tonnes per year).

2.4.- Sachtleben production unit at Duisburg

(Annual production capacity (sulphate process) : 55 000 t)

- Weak acid effluent

Installation of a number of integrated water cycles has substantially reduced the sulphur and iron content of the effluents. In all the pollutant (i.e. sulphur and iron) load has been reduced by approximately 64%.

- Discharges to the atmosphere

Three-stage purification of the untreated off-gases has reduced the pollutant load by some 92 %, or by 300 tonnes a year.

## 6.5.- UNITED KINGDOM

Data were received for three production plants, one of them - the BTP Tioxide plant at Greatham - discharging into the Tees estuary, the other two - the BTP Tioxide plant at Grimsby and the Laporte Industries plant at Stallingborough - into the Humber estuary. All operations at BTP's Billingham plant, which previously also discharged into the Tees estuary, ceased in 1981.

### 6.5.1.- BTP Tioxide plant at Greatham

(Annual production capacity : 50 000 t)

The Greatham works treats rutile by the chloride process. There is therefore no waste problem with copperas.

#### Strong acid effluent

- a) Each day 5 000 cubic metres of acid effluent is discharged direct into the estuary from the holding and settling pond, though only when the tide is falling.

The following improvements are to be made before 1 July 1987 :

- (i) installation of larger filter units to reduce the volume of titanium dioxide discharged (completed in 1981);
- (ii) subdivision of the buffer pond into two compartments - one for exploitation and one for purification - for more thorough settling out of the titanium dioxide (completed in 1980).
- b) Effluent containing hypochlorite arises when the off-gases are scrubbed with caustic soda and is subsequently discharged into the aquatic environment, though not at the same time as the acidic waste referred to in paragraph (a); a maximum of 10 cubic metres is discharged each hour.

Now installation of a catalysis unit to convert the sodium hypochlorite into sodium chloride will put a stop to the sodium hypochlorite discharges. Hypochlorite production is expected to reach 10 000 tonnes per year in 1985, though only 3 000 tonnes a year is reused at the moment. Sales of 6 000 tonnes a year are expected in 1985.

#### 6.5.2.- BTP Tioxide works at Grimsby

(Annual production capacity : 100 000 t)

BTP Tioxide's Grimsby works treats ilmenite by the sulphate process.

#### Strong acid effluent

At the moment a 1 000 m outfall continuously discharges a maximum of 25 000 m<sup>3</sup> of acid waste with a pH of 1 direct into the Humber estuary each day.

The precise improvements to be made will be decided by the results of a research programme which is to assess the relative merit of the following options by the end of 1982 :

- (i) construction of land-based storage facilities in the short term to obviate the need for discharges during slack water periods;
- (ii) specially-designed diffusers for the outfall;
- (iii) relocation of the point of discharges from the outfall;
- (iv) a combination of all three.

A work programme based on those findings and on the respective cost-benefit ratios will then be carried through and completed in 1986. Finally, by July 1987 a suitable biochemical programme will be devised to monitor the success of the measures proposed above.

### Solid waste

Every year 40 000 t of copperas is separated out and reused in order to reduce the load in the acid effluent. The remainder is discharged into the estuary. Studies into new potential applications are still in progress.

No specific details of the other types of discharges were given.

### 6.5.3.- Laporte Industries plant at Stallingborough

(Annual production capacity : 94 000 t)

Both the sulphate and chloride processes are applied at Stallingborough.

### Strong acid effluent

Together the two processes result in approximately 38 000 m<sup>3</sup> of effluent with a pH of 1 being discharged continuously into the Humber estuary at Immingham each day, from a 50 m outfall.

The improvements to be made are the same as those planned at BTP Tioxide's plant at Grimsby. No specific details of the other types of discharge were given.

### Solid waste

Each year 30 000 t of the copperas residues from the sulphate process are reused; the remainder is discharged into the estuary along with the acid effluent. Studies into new potential applications for the copperas are now in progress.

As for discharges to the atmosphere, the United Kingdom authorities gave details of the presumptive limits for each pollutant.



## 6.6.- BELGIUM

The Commission received data on two plants, as follows :

### 6.6.1.- NL Chemicals unit at Ghent

(Annual production capacity : 40 000 t)

The Ghent plant employs the sulphate process, with high-grade (70 %) ore as the feedstock.

#### Strong acid effluent

Some of the strong acid wastes are dumped at sea, though only with official approval.

#### Weak acid effluent

The weak acids are discharged into the Ghent/Terneuzen canal, which flows into the River Escaut. A technical study of the viability of fitting the works with a purification plant is now in progress.

#### Solid waste

The insoluble unreacted ore and the filter residues are neutralized and stored on land, at a dump reserved for this purpose. The statutory limits on the height of the dumps for this solid waste are to be revised.

### 6.6.2.- Bayer plant at Antwerp

(Annual production capacity : 26 000 t).

This plant likewise employs the sulphate process with high-grade (70 %  $TiO_2$ ) ore as the feedstock.

#### Strong acid effluent

The strong acid effluent is pumped into the North Sea, subject to official authorization.

#### Weak acid effluent

Weak acids are treated in a purification unit and then discharged into the Escaut.

## Solid waste

The insoluble non-reacted ore is dumped at sea, along with the acids.

The Belgian authorities pointed out that the cost of the construction of an  $H_2SO_4$  and iron recovery unit was so high that the Ghent unit would no longer remain competitive if they were built under the present circumstances. Nevertheless studies were in hand.

As for the Bayer plant at Antwerp, there had been plans to treat the strong acid effluent at the Uerdingen plant (in Germany), but these had been abandoned since the latter was already operating at full capacity. In the light of the experience already gained in Germany, studies were now under way at the Antwerp unit to assess the real prospects for using the other plant.

Finally, Belgium's titanium dioxide industry has been instructed to treat high-grade ores exclusively. The limits laid down in the dumping licences will preclude treatment of ilmenite. One final specific condition which has been proposed is that ferrous sulphate should be dumped in solution only, i.e. without suspended particulates.

## 7.- OPTIONS AVAILABLE FOR THE TREATMENT OF LIQUID WASTES WITH A VIEW TO THE PROGRESSIVE REDUCTION AND ULTIMATE ELIMINATION OF POLLUTION

Most of the pollution caused by the liquid discharges is attributable to the sulphate process and to the starting ore used.

The methods for reducing and eliminating pollution caused by these discharges fall into five categories :

- neutralization
- recovery of the spent acid
- physico-chemical treatment
- roasting of the ferrous sulphate
- appropriate technology.

### 7.1.- Neutralization

This process removes the sulphuric acid and the metal sulphates from the weak acid and strong acid effluents.

Following neutralization by chalk or limestone, the supernatant liquid - the volume of which is equivalent to that of the effluent treated - is discharged, at a pH of about 7, into the aquatic environment.

The sludge left over from the neutralization process contains metal hydroxides and gypsum and is a solid waste which must be stored on land at appropriate sites or discharged at sea. Little energy is consumed in this process. The costs for the neutralization unit can add about 10 % to the selling price for the end-product.

### 7.2.- Recovery of spent acid

This process can be applied only to the mother liquors, i.e. to acid effluent containing between 20 and 23 % free sulphuric acid and small quantities of all the metals whose oxides are taken up in solution during the chemical breakdown of the ore.

The weak acid effluents are too dilute to be suitable for such treatment.

The principle of the process is to concentrate the acid to 65 % in two stages, as follows :

- concentration to 35 % sulphuric acid followed by separation of the ferrous sulphate after crystallization;
- concentration to between 35% and 65% and further separation of the crystallized ferrous sulphate.

This method is preferable to direct concentration to 65 % on account of the problems otherwise caused by the solubility and separation of the sulphates at the end of the process.

The final stage would be to concentrate the sulphuric acid beyond 65 %. The problems in this final stage are that dissolved salts are precipitated during the concentration of the acid and the prohibitive energy consumption cost. The concentrated acid can be recycled directly for the first stage of the titanium dioxide manufacturing process, i.e. for the chemical digestion or breakdown of the starting ore.

If the mother liquors are reconcentrated, a parallel unit is also needed to treat the sulphates produced.

### 7.3.- Physico-chemical treatment methods

Processes such as membrane separation (e.g. dialysis or reverse osmosis) and the electro-chemical methods are of very limited effectiveness.

#### 7.4.- Roasting of the ferrous sulphate

If ilmenite is the starting ore, some three tonnes of ferrous sulphate are produced, i.e. one tonne of sulphuric acid is bound, for each tonne of  $TiO_2$  produced.

This process regenerates the bound acid and produces iron oxide which can be used by the metals industry.

Calcination of the monohydrate ferrous sulphate produces a pigment which is suitable for use in paints and glosses.

#### 7.5.- Appropriate technology

The first stage in any clean technology would be to use an ore with a higher  $TiO_2$  content (of the order of 85 % rather than 70 % ore or than ilmenite).

Supplies of this grade of ore are governed by current contracts, which conditions in the producer country and the slag production capacity, which covers no more than 85% (400 000 t/yr) of the potential market demand.

Apart from the raw materials supply problem, the best production process is the chloride process.

### 8.- METHODS FOR THE TREATMENT OF GASEOUS DISCHARGES

Various stages of the titanium dioxide manufacturing process generate gas emissions which generally consist of sulphur or chlorine compounds and dust.

- With the sulphate process, atmospheric emissions are a direct result of  $TiO_2$  production and originate from two main sources, namely the towers where the ore is digested and the calcination kilns.
- The ore crushing and drying plants must be fitted with sleeve filters to recover the dust.

- The gases given off during the chemical reaction between the sulphuric acid and the ore contain air, water vapour,  $\text{SO}_2$  and  $\text{SO}_3$ . The reaction thermodynamics are such that a substantial amount of gas is released during the few minutes chemical breakdown.

Scrubbing towers remove the acid droplets. The scrubbing water is generally channelled towards the weak acid effluent so that both can be neutralized prior to discharge into the aquatic environment. Neutralization with caustic soda also helps to clean the off-gases.

- The off-gases emitted during calcination are passed through scrubbing towers where most of the solid particles are removed; they are then passed through wet electrostatic precipitators to reduce the  $\text{SO}_3$  level. Further improvements could be made by using an alkaline scrubbing medium.

## 9. COMMENTS ON THE PROPOSAL FOR A DIRECTIVE

### 9.1. Procedure for formulating the proposal

The Commission called together a group of advisers, chaired by a Commission representative, to analyse the programmes and to give its opinion on their technical and scientific merits.

The advisers received details of the programmes submitted by the Community's  $\text{TiO}_2$ -producing countries and outlined their conclusions at the group's meeting on 9 and 10 February 1982. At the same meeting they examined the data submitted for each individual plant and proceeded to analyse them, and the experts' conclusions, in depth.

The Commission also called a meeting of the Member States' national experts on 18 and 19 October 1982, to outline the advisers' conclusions to them and to let them know the main lines of action which the Commission intended to follow in implementation of Article 9 of the basic Directive. In the light of talks with the industrial circles concerned, the Commission has now drafted this proposal.

The Commission has taken care to ensure that the industrial data gathered and duly passed on to the experts and advisers are kept secret, as laid down in Article 13(3) of the basic Directive.

## 9.2. Aims of the proposal

The technical procedure proposed for harmonizing the programmes for the reduction and eventual elimination of pollution takes account of:

- (i) the interim targets to be achieved;
- (ii) the appropriate waste treatment systems;
- (iii) the processes or technologies already available, or now under development in certain Member States.

With certain Member States suggesting, or already employing, different technology to implement the basic Directive with a view to the reduction and eventual elimination of this form of pollution, and with the level of investment already, or now being, made to achieve this target differing from one Member State to another, the Commission has been forced to harmonize the national pollution reduction programmes already completed, now under consideration or currently under way.

Consequently, the Commission proposal is a balance between the objectives defined in the basic Directive and the Member States' national programmes. It allows exemptions from the proposed timetable should technological problems arise.

The Commission is well aware of the technical and economic considerations to be borne in mind by the Community's titanium dioxide industry when striving to comply with this proposal for a Directive on a European scale in today's economic climate.

For this reason, it has drawn up a timetable ranging from four and nine years in duration, depending on the case in point, to allow the industry to make the investment needed to achieve the objectives set by the Council Directive of 20 February 1978 on waste from the titanium dioxide industry.

### 9.3. Comments on the individual Articles in the proposal for a Directive

The aim of this Directive is the prevention and progressive reduction, with a view to its elimination, of pollution caused by waste from the titanium dioxide industry.

Existing industrial establishments must be fitted with appropriate systems for treating the various wastes arising so that following treatment the discharges of liquid, solid and gaseous wastes do not exceed the percentage and reference values specified. This requirement amounts, therefore, to a significant reduction in the level of pollution. The remainder may be discharged under the usual conditions, subject to compliance with Directive 78/176/EEC.

Beyond that, the timetable mentioned in various Articles of this proposal is designed to allow the industries to make the adjustments under realistic economic and technical conditions. It is clear from the pollution reduction programmes sent to the Commission that anti-pollution systems had been set up in the Member States even before the basic Directive entered into force on 22 February 1979.

Since two manufacturing processes are employed, each with a different impact on the environment in general, they are dealt with separately.



### 9.3.1. Sulphate process

- (a) The idea is to prohibit dumping of  $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$  "copperas" - in all its forms (i.e. whether solid, in suspension or re-dissolved in the mother liquors) in estuary waters, coastal waters and in the open sea by 1 July 1987.

First, the Commission recalls that Directive 78/176/EEC requires the Member States to take appropriate measures to encourage the prevention, recycling and processing of waste, the extraction of raw materials and any other process for the re-use of waste.

Secondly, it feels that the dumping of copperas damages the aquatic environment through its detrimental side-effects such as the reduction in the oxygen content of the water, the secondary physico-chemical reactions sometimes involving other metals where they too are precipitated, the reduced plankton population and the deposits of materials on the sea bed and the consequent reduction in phytoplankton and fish larvae production.

At present between 40% and 50% of the volume of copperas arising is re-used once it has been separated out - the volume varying from one Member States to another - with ilmenite, the starting ore. The remainder is stored at suitably-equipped dumps.

Plants in some Member States avoid formation of this by-product altogether by turning to higher-grade ores, thus obviating the need either to dump copperas in the aquatic environment or to re-use it.

Finally, one Member States said that it would dump no more copperas at sea after 1 July 1987 and that it even hoped to attain this objective as early as 1984.

- (b) Dumping of the insoluble matter left after dissociation of the ore is to be prohibited with effect from 1 July 1987; at present most production units wash, neutralize, store and re-use these materials.

As in paragraph (a), the Commission again draws attention to the requirements of the Directive and feels that certain dumping conditions and the composition of these insoluble materials can result in harm to the aquatic environment through the impact of the increased turbidity of the water on marine organisms, the deposits of material on the sea bed eventually forming a layer to the detriment of the invertebrate populations, the reduction, the penetration by sunlight and the consequent decrease in primary production and in the plankton population.

One Member State said that this insoluble waste was to be stored on land after 1 July 1987.

- (c) On discharges of liquid wastes, the proposal sets a reference value to be attained by 1 July 1988 - 1 000 kg of free acid per tonne of titanium dioxide produced. This value amounts to a ban of dumping of all strong acid wastes and thus fits in with one of the objectives of Article 9(3). Strong acid is the liquid waste left after the separation phase which follows on from the hydrolization of the titanium oxide and containing between 20% and 23% free sulphuric acid plus salts of metals such as Ti, Fe, Cr, Ni, Zn, Pb, Mn, V, whether dissolved or in suspension.

The Commission feels that these liquid wastes have a deleterious impact on the aquatic environment, partly because of their intrinsic acidity and partly because of their composition.

What is more, they also have a detrimental impact on sessile benthic fauna and on the marine flora. Account must also be taken of the synergistic effects between certain metals.

The quantity of free acid, in the form of sulphuric acid, arising from the weak and strong acids has been taken as the reference value for liquid effluents.

From the data submitted by the Member States and from the bilateral meetings between the Member States and the Commission, it appears extremely difficult to allow for the different sources of the liquid effluents and, above all, for the mixing thereof prior to dumping in the aquatic environment.

The data submitted show that some production units automatically separate the acid from the wash water and recycle or treat the effluent in order to cut down the volume of acid waste and to reconcentrate it.

Finally, the volume of concentrated sulphuric acid needed to break down the ore depends on the feed ore. No plant-by-plant approach was contemplated since the feed ore used depends on supply conditions; and some Member States even failed to specify the ore processed.

- (d) The proposed 60% further reduction in the reference value (1 000 kg of free acid per tonne of titanium dioxide produced) by 1 July 1993 is based, above all, on the fact that several production units dump no acid solutions at all in the aquatic environment and recycle part of the acid.

In today's economic climate and judging from the technical forecasts available, the Commission feels that this percentage can be attained by the proposed deadline. This reduction would mark a significant cut back in the level of pollution.

- (e) Dumping of liquid wastes at above 30°C in coastal waters and estuaries is to be prohibited with effect from 1 July 1988.

The Commission feels that significant temperature differences between the effluent and the receiving waters could lead to thermal stratification in the dumping areas which will impede the dilution and mixing process. Finally, the increase in the ambient temperature might put certain organisms at risk.

- (f) In surface water (fresh water), the dumping of liquid wastes with a pH lower than 6.5 and at above 30°C is to be prohibited with effect from 1 July 1988. Some of the industrial plants which discharge their liquid wastes into water courses already satisfy these conditions overall; some pay a levy proportional to the damage potential of the liquid wastes which they discharge.

To prevent liquid wastes from damaging the aquatic environment, the Commission feels that they should be dumped only under clearly-defined conditions and in particular that acid solutions should be allowed subjected to settlement and neutralization prior to discharge.

Finally, the dumping of liquid wastes at excessive temperatures can impair the properties of the water, for example by reducing its oxygen content and affecting the speed of chemical and biochemical reactions.

- (g) Discharges into the atmosphere will all be subject to the same reference value of 30 kg of SO<sub>x</sub> per tonne of titanium dioxide produced.

The definition of the limit value for SO<sub>x</sub> allows due account to be taken of the sources of both sulphur dioxide and sulphur trioxide.

Today some plants already achieve a value of between 33 kg and 35 kg or so per tonne of titanium dioxide produced; the Commission therefore feels that the lower value can be attained by the date proposed.

### 9.3.2. Chloride process

Compared with the previous process, the chloride process gives rise to far less liquid effluent and pollution.

- (a) The reference value stipulated for 1 July 1988 - 200 kg of acid per tonne of titanium dioxide produced - is the maximum which may by that date be dumped in estuary waters, coastal waters and in the open sea.

The Commission feels that this value can be attained by the set date and will reduce the damage which these wastes cause to the aquatic environment.

- (b) Where liquid effluents are discharged into surface water, a pH of 6.5 must be observed to avoid harmful side-effects on water flora and fauna, as described above.
- (c) As regards chlorine discharges into the atmosphere, the reference value to be attained by 1988 - 6 g per tonne of titanium dioxide produced - will allow a reduction in this category of waste.

It should be pointed out that the Commission received less information on this process than on the sulphate process.

### 9.3.3. Other Articles

The other Articles in the proposal cover the following main points:

- (a) The prospects for storing on land the various by-products arising from the manufacturing process or from treatment of the wastes under certain conditions.

(b) Arrangements for exemptions from the set timetable should technical problems arise on application of the appropriate technologies.

10. CONSULTATION OF THE EUROPEAN PARLIAMENT AND OF THE ECONOMIC AND SOCIAL COMMITTEE

Since this proposal for a Directive is based on Article 9 of Directive 78/176/EEC, it is compulsory to consult the European Parliament and the Economic and Social Committee, as required by paragraph 3 of that Article.

Proposal for a  
COUNCIL DIRECTIVE

on procedures for harmonizing the programmes for the  
reduction and eventual elimination of pollution caused  
by waste from the titanium dioxide industry

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THE COUNCIL OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Economic Community, and in particular Articles 100 and 235 thereof,

Having regard to the proposal from the Commission,

Having regard to the opinion of the European Parliament,

Having regard to the opinion of the Economic and Social Committee,

Whereas Article 9 of Council Directive 78/176/EEC of 20 February 1978 on waste from the titanium dioxide industry <sup>1</sup>, as last amended by Directive 83/29/EEC<sup>2</sup>, requires the Member States to draw up programmes for the progressive reduction and eventual elimination of pollution caused by waste from industrial establishments in existence on 20 February 1978;

Whereas these programmes, duly submitted to the Commission, set general interim targets for the reduction of pollution from liquid, solid and gaseous wastes to be achieved by 1 July 1987; whereas the Commission is required to submit proposals for the harmonization of these programmes with regard to the reduction and eventual elimination of this pollution and the improvement of the conditions of competition in the titanium dioxide industry ; whereas the Council is required to act on these proposals within six months of the publication of the opinion of the European Parliament and that of the Economic and Social Committee in the Official Journal of the European Communities;

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<sup>1</sup> OJ L 54, 25.2.1978, p. 19

<sup>2</sup> OJ L 32, 3.2.1983, p. 28

Whereas in order to protect the aquatic environment dumping of copperas and of insoluble matter should be prohibited and discharges of liquid wastes from the manufacturing processes, and in particular of strong acids, should be reduced in view of their harmful effects;

Whereas in order to protect the aquatic environment liquid wastes should be discharged into surface waters only under specified conditions of temperature and neutrality;

Whereas it is necessary to fix in respect of gaseous discharges from the manufacturing processes reference values designed to have a long-term preventive effect with regard to health and environmental protection;

Whereas existing industrial establishments must employ the appropriate systems for treating the wastes in order to attain the requisite levels by the set dates;

Whereas since installation of the appropriate systems can give rise to delays in the application of the measures to harmonize the programmes, provision must be made for derogation from this Directive in certain cases, subject to the prior agreement of the Commission;

Whereas the provisions of this Directive do not prejudice the obligations placed on Member States by Council Directives 80/68/EEC of 17 December 1979 on the protection of ground water against pollution caused by certain dangerous substances (1) and 80/779/EEC of 15 July 1980 on air quality limit values and guide values for sulphur dioxide and suspended particulates (2);

Whereas, since all the requisite powers have not been provided for by the Treaty, Article 235 of the Treaty should be invoked,

HAS ADOPTED THIS DIRECTIVE:

(1) OJ No L 20, 26.1.1980, p. 43

(2) OJ No L 229, 30.8.1980, p. 30



Article 1

This Directive lays down, as required by Article 9(3) of Directive 78/176/EEC, procedures for harmonizing the programmes for the reduction and eventual elimination of pollution from existing industrial establishments and is intended to improve the conditions of competition in the titanium dioxide industry.

Article 2

1. For the purposes of this Directive:

"Liquid wastes" means:

- in the case of the sulphate process:
  - . strong acid arising from the separation phase which follows on from the hydrolysis of the titanium oxide solutions and containing between 20% and 23% free sulphuric acid and various metallic salts; and
  - . weak acid, at a concentration of between 5% and 7%, arising from the washing phase which follows on from the separation stage and also the other wash waters, and in particular those associated with the gaseous discharges from the manufacturing processes, including both the sulphate and chloride processes;
- in the case of the chloride process:
  - . free hydrochloric acid.

"Reference value" means:

- for liquid wastes:

. in the case of the sulphate process:

the quantity of free acid, in the form of sulphuric acid, arising from the strong acids and/or weak acids containing, whether dissolved or in suspension, salts of metals such as Ti, Fe, Cr, Ni, Zn, Pb, Mn, V, arising from the manufacturing process, with the exception of copperas;

. in the case of the chloride process:

the quantity of free acid in the liquid wastes in the form of hydrochloric acid containing metal chlorides;

- for  $SO_x$ :

. in the case of the sulphate process:

the quantity of sulphur dioxide, and of sulphur trioxide expressed as  $SO_2$  equivalent, arising from the digestion towers and calcination kilns plus the acid droplets;

- for chlorine:

. in the case of the chloride process:

the quantity of chlorine arising from the various stages of the manufacturing process.

"Copperas" means:

crystallized ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) separated out in solid from the titanyl sulphate solution.

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"Insoluble matter" means:

products which are not broken down by the sulphuric acid during the manufacturing process.

2. Terms defined in Directive 78/176/EEC have the same meaning for the purposes of this Directive.

### Article 3

1. This Article shall apply to existing industrial establishments employing the sulphate process.
2. Member States shall take the necessary measures, including those relating to the installation of appropriate waste treatment systems, to ensure that:

in respect of estuary waters, coastal waters and the open sea:

- by 1 July 1987 they prohibit discharges of all forms of copperas and of insoluble matter;
- by 1 July 1988 they reduce discharges of liquid wastes to the reference value of 1 000 kg of free acid per tonne of titanium dioxide produced;
- by 1 July 1993 they further reduce discharges of liquid wastes by 60% of the abovementioned reference value ;

in respect of coastal waters and estuary waters, by 1 July 1988 they prohibit discharges of liquid wastes at above 30°C.

3. In respect of surface waters, by 1 July 1988 the Member States shall prohibit discharges of liquid wastes at above 30°C and with a pH value lower than 6,5.

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4. (a) In respect of the atmosphere, Member States shall take the measures necessary to ensure that by 1 July 1988  $SO_x$  discharges are reduced to the reference value of 30 kg per tonne of titanium dioxide produced, as the annual average.
- (b) The provisions of this Directive shall not prejudice Directive 80/779/EEC.
- (c) The reference method of measurement for  $SO_x$  emissions is set out in the Annex.

Article 4

1. This Article shall apply to existing industrial establishments employing the chloride process.
2. Member States shall take the necessary measures, including those relating to the installation of appropriate waste treatment systems, to ensure that:
- in respect of estuary waters, coastal waters and the open sea, by 1 July 1988 discharges of liquid wastes are reduced to the reference value of 200 kg of acid per tonne of titanium dioxide produced;
  - in respect of surface waters, by 1 July 1988 they prohibit discharges of liquid wastes with a pH value lower than 6.5.

They shall prohibit discharges of all solid wastes such as filtrates and metal chlorides into these same waters.

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3. In respect of the atmosphere, Member States shall take the measures necessary to ensure that by 1 July 1988 chlorine emissions are reduced to the reference value of 6 g per tonne of titanium dioxide produced.

Article 5

Member States shall monitor the reference values, reductions and prohibitions specified in Articles 3 and 4, in relation to the actual production of each establishment.

Article 6

1. Member States shall take the measures necessary to ensure that:
  - wastes subject to a discharge prohibition are stored on land with a view to re-use wherever possible;
  - products arising from the treatment of copperas, strong acids, weak acids and any other wastes not subsequently re-used can be stored on land without prejudice to Directive 80/68/EEC.
2. The remaining quantities of the discharges defined in Articles 3 and 4 may be disposed of without pretreatment.

Article 7

1. Subject to prior agreement by the Commission, a Member State may depart from the set timetable should technical problems arise during the application of the appropriate technologies.

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2. The Member State concerned shall send to the Commission all the detailed supporting documents which the Commission needs to decide whether the conditions for applying paragraph 1 have been satisfied.
3. Extensions of the period for each category of waste may not exceed twelve months.

Article 8

1. Member States shall take the measures necessary to comply with this Directive not later than 1 January 1986. They shall forthwith inform the Commission thereof.
2. Member States shall communicate to the Commission the provisions of national law which they adopt in the field governed by this Directive.

Article 9

This Directive is addressed to the Member States.

Done at Brussels,

For the Council

The President

## A N N E X

### Principle of the reference method of measurement for gaseous SO<sub>x</sub> emissions

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For the purposes of calculating the quantities of SO<sub>2</sub>, and of SO<sub>3</sub> and acid droplets expressed as SO<sub>2</sub> equivalent, discharged by specific installations, account must be taken of the volume of gas discharged over the duration of the specific operations in question and of the average SO<sub>2</sub>/SO<sub>3</sub> content measured over the same period. the SO<sub>2</sub>/SO<sub>3</sub> flow rate and content must be determined under the same temperature and humidity conditions.