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A SURVEY OF THE METAL FINISHING INDUSTRY IN THE CITY AND METROPOLITAN AREA OF SAO PAULO IN THE STATE OF SAO PAULO, BRAZIL, IN ORDER TO ADVISE ON THE REDUCTION OF POLLUTION CAUSED BY THAT INDUSTRY TO THE RIVER TIETE

SI/BRA/93/801/11-01/J13102

A TECHNICAL REPORT PREPARED BY

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ABSTRACT

A SURVEY OF THE METAL FINISHING INDUSTRY IN THE CITY AND METROPOLITAN AREA OF SAO PAULO IN THE STATE OF SAO PAULO, BRAZIL, IN ORDER TO ADVISE ON THE REDUCTION OF POLLUTION CAUSED BY THAT INDUSTRY TO THE RIVER TIETE

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The object of the survey was to establish how the metal finishing industry could reduce or eliminate the discharge of heavy metals and other toxic substances in its effluent and also advise on the recovery of metals and chemicals. The UNIDO expert visited a number of electroplating enterprises in the city and metropolitan area of Sao Paulo and also enterprises in other towns in the State of Sao Paulo, whose effluent discharges either directly or indirectly, via the sewage system, into the Rio Tiete. Discussions were held with, and visits made to, the water supply and treatment organisation, SABESP, the environmental organisation of the Government of the State of Sao Paulo, CETESB, the Government body dealing with scientific, technological and economic development in the State of Sao Paulo, SCTDE and the association of the metal finishing industry in Sao Paulo, SINDISUPER. The duration of the visit to Sao Paulo was six weeks. At the end of the visit, a presentation was made to SINDISUPER, and discussions were held at the offices of SCTDE with the UNIDO experts, a representative of SINDISUPER, UNIDO staff members, a representative of IPT and the SCTDE officers dealing with the project

The UNIDO metal finishing expert found good technical management in the metal finishing industry and the quality of the work produced was of a high standard Nearly all the enterprises visited had built, or were building effluent treatment plant of the conventional type and were also making efforts to reduce their consumption of water. However, in too many cases the housekeeping of the factories was not as good as it should be which will make it difficult to meet the stringent effluent discharge limits set by CETESB The industry in Sao Paulo will find it difficult to recover the component metals and chemicals from the filtercake produced by the effluent treatment process because it does not appear to have looked in any detail at the more modern methods of effluent treatment, namely, electrolytic recovery and ion exchange. To effect this separation from metal finishing filtercake will need some development work as there do not appear to be any general methods of recovery except in a few cases in the USA

It was recommended that the industry should continue to work to reduce water consumption, establish operator training, look further into separating rinse lines to simplify the separation and extraction of heavy metals

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INTRODUCTION

The City and Metropolitan area of Sao Paulo is estimated to have the second greatest population in the world, probably in excess of 17 million people. It is the largest industrial centre in Brazil, and is probably the largest manufacturing area in South America. The Rio Tiete flows through the City of Sao Paulo and is heavily contaminated with both domestic and industrial waste. It flows westward until it meets the Rio Parana. This river flows South, joining the Rio Paraguay and flowing into the sea between Buenos Aires and Montevideo.

At present, less than 50% of the domestic sewage being discharged to the Rio Tiete is treated and the river also receives a large amount of untreated industrial waste. To try to reduce this problem the Government of the State of Sao Paulo plans to improve the collection of municipal sewage and treating at least 60% of it before discharging it to the river. The Government agency dealing with this project is the Secretaria da Ciencia, Tecnologia e Desenvolvimento Economico (SCTDE) do Estado de Sao Paulo and it has identified the electroplating industry and the textile dyeing and finishing industry as among the most serious industrial polluters. There are between 400 and 500 registered companies which carry out electroplating and it is estimated that there are at least an equal number of smaller companies , which are non registered and which are electroplating in a semi-legal manner.

The Government of Sao Paulo sought the assistance of UNIDO to find a Metal Finishing expert to look at the activities of the metal finishing industry and to comment on the contribution the metal finishing industry was making to the pollution of the Rio Tiete by discharging heavy metals as well as undesirable anions, such as cyanides, to the sewers, or directly into the river. Further, he would advise both individual firms and the Government of the situation as he found it and advise on how to proceed.

The terms of reference and the duties of the expert are set out in detail in Annex 1. J K Cosslett was appointed to carry out this work and he arrived in Sao Paulo on 23 August 1993 for a six week mission.

The object of the mission was to

a) survey a cross section of metal finishing companies,

b) classify them by size, types of work and nature of finishing waste.

c) Make recommendations for improvement of technologies by relatively low investments and simple technology modifications to try to reduce chemical consumption and discharge of pollutants.

d) Make recommendations for in situ treatment of waste streams and the recycling of heavy metals and chemicals

e) Recommend on collection of different types of waste for centralized treatment, recycling of heavy metals and chemicals and the safe disposal of residues.
f) Advise on the establishment of centralised treatment of sludges and other wastes, and advise on cooperation between plants to treat similar wastes from different plants in the proposed central treatment facilities on a toll basis.
g) Recommend criteria for relocation of metal finishing companies to a specialised industrial estate.
h) Prepare guidelines for the infra structure of the proposed metal finishing estate.

Preliminary discussions were held between J K Cosslett and SCTDE and the leading members of SINDISUPER at the very beginning of the project in which it was discussed how matters should proceed. Visits were made to IPT, the Institute of Technological Research, CETESB, the environmental agency which sets the effluent limits, SABESP, the water company responsible for the supply of water and the treatment of waste water, and the metal finishing department of the SENAI school Mario Amato. A number of visits were made to plating shops of different sizes. However the largest part of electroplating in Sao Paulo is zinc plating so that there was not the variety of processes that might be expected in an industrial city the size of Sao Paulo.

J K Cosslett held a seminar with a members of SINDISUPER at the end of his visit in which he gave a lecture on his findings and suggestions for the future, the main one being that although the quality of work produced was generally of the highest order, the housekeeping of many of the plating shops was not good and until that was improved reaching the stringent effluent targets set by CETESB would be difficult.

On the penultimate day of J K Cosslett's visit, a review was held of the project between J K Cosslett, David Brewer the UNIDO water treatment expert, Dr Tamas Grof, the UNIDO Backstop Officer, Dr Klaus Billand, UNIDO Country Director, Mr Marco Barbieri, SINDISUPER and Officers of SCTDE. Discussion covered the proposal for using the metal finishing filtercake as a mixture in cement manufacture, which has been proposed by members of the metal finishing industry, the possibility of metal recovery from the filtercake, and the possibility of siting metal finishing organisations together on specialist estates.

Of the original objectives, it has not been possible to give categoric recommendations for the last three because not sufficient is known about these approaches as they are brand new concepts. However guidelines have been laid down on how to proceed in these investigations

I. THE VISITS TO TECHNICAL INSTITUTIONS, SUPERVISING ORGANISATIONS AND METAL FINISHING COMPANIES

The preliminaries of this assignment were two visits to the Government offices in the first week to meet the Government representatives of SCTDE who were assigned to the project, the representative of SINDISUPER. the syndicate of metal finishing firms , and a representative of IPT, The Institute of Technological Research. who are also involved in the project and also who were supplying the interpreters. Their names and functions are given in Annex 2

A Technical Institutions

The Institute of Technological Research, IPT

The involvement of this organisation is through the Metallurgy Department and particularly the Corrosion and Metal Finishing section under Dr Zehbour Panossian. Dr Panossian is a member of SINDISUPER This department carries out research into these two subjects and also conducts investigations into corrosion failure on behalf of clients. This department has the resources and personnel to become involved in any academic, development and experimental work that may be necessary in the metal finishing aspects of the pollution of the Rio Tiete. Dr Panossian has submitted a provisional plan of action for tackling the overall problem of metal finishing contamination of Rio Tiete to SINDISUPER.

The SENAI School Mario Amato

This technical school is situated in Sao Bernado do Campo just outside Sao Paulo on an estate containing modern factories and is itself a modern school. The school is funded by industry for the training of 16 to 19 year old students or perhaps a little older. At the end of the three year course, the students are ready to go into industry or on to higher education.

A tour of the chemistry department was made in which was shown the system of linked lecture theatres and demonstration areas and this excellent system was repeated for inorganic, organic and physical chemistry teaching as well as for training in analytical chemistry. Associated with the chemistry department was the metal finishing demonstration area. This was quite superb and it was everything a well laid out plating shop should be. The demonstration tanks and barrel plating units were smaller than would be seen in a commercial plating shop because they were primarily used as training baths. Every method of finishing , namely electroplating, electroless plating. painting and powder coating. conversion

coatings, anodising and dyeing could be demonstrated as well as rinsing, counter current rinsing and spray rinsing included, and pretreatments.

The students are taught Faraday's laws of electrolysis and their application to electroplating. In addition they are taught that not all electrodeposits are deposited with 100% efficiency. They are also taught about throwing power in the electroplating process and the importance of accurately measuring surfaces to be electroplated and calculating the current required in order to deposit the amount of metal required, not too thick and not too thin.

A conventional effluent treatment plant was about to be commissioned which has full instrumental control, namely pH and millivolt control for the treatment of hexavalent chromium rinses and cyanide rinses. The supervisor, Mr Cesta does not stop there, he makes up artificial effluents upon which the students carry out experiments. They are asked to add a large excess of sodium hydroxide to one sample, and add sodium hydroxide dropwise in a controlled manner to the other sample to demonstrate the effect of uncontrolled additions has on the precipitation and flocculation of metal hydroxides.

This is a most impressive metal finishing training unit, certainly the best ever seen by J K Cosslett and it is difficult to believe that there is any better in the world. This is a facility of which the metal finishing fraternity must take full advantage for training workers and even refresher courses for management.

B. Supervising Organisations

The main supervising bodies in the discharge of water are CETESB and SABESP. Both of these organisations were visited for discussions later on in the assignment.

CETESB

This is the environmental arm of the Government of the State of Sao Paulo and it is empowered to set the limits of discharge of contaminating materials to the rivers and sewers. Three visits were made to the offices of this organisation. The first visit was to see the organisation and its facilities. It is very well equipped with the latest testing and analytical equipment and has the quality of staff which can make use of the facilities. This organisation is clearly able to back up its legal powers with technical expertise and will be well able to find organisations which discharge metals and other materials to the water courses and sewers above their legal limits

The second and third visits were continuations of the first visit and were made in order to obtain more detail on discharge limits to the water courses and the thinking of CETESB concerning the disposal of filtercake. The limits of discharge are set out in Annex 4 The current estimates of discharge to the Rio Tiete are given in Annex 3 The sampling plans used will depend on how good a company is on a) controlling its discharge, b) the size of the discharge and c) the size of the industry. Initially there will be 24 hour sampling . Once CETESB has confidence in a company they will reduce the frequency of sampling . It is intended that eventually firms will be responsible for their own sampling and analysis.

The final visit to CETESB was to discuss the solid waste problem. CETESB say that the metal finishing industry can use landfill outside the city of Sao Paulo but they have to pay for it themselves. On the question of using the filtercake for incorporating into cement, CETESB of Sao Paulo have not given permission because the cement industry have not demonstrated to the satisfaction of CETESB that it works. However the CETESB of Parana state have given permission.

CETESB have looked at 200 plating firms and know all their processes , waste water discharge and analysis

SABESP

This is the water company responsible for the supply of potable water to the City and Metropolitan area of Sao Paulo and also for treatment of waste water and discharging it in a satisfactory condition to the Rio Tiete Two visits were made to SABESP, the first to the administrative headquarters to outline the function of SABESP and later to one of the water treatment plants and then to a pumping station The second visit was to a new sewage works.

C. Metal finishing Companies

In the course of this assignment, 19 enterprises were visited which were either wholly or partially involved with electroplating. In a few cases repeat visits were made in order to clarify detail and for further discussion Broadly speaking the companies seen could be divided into those which only carry out sub contract work for outside customers, and those companies which carry out 'in house' plating, that is, the only electroplating they do was for their own products. Those companies visited which only carry out 'in house' electroplating were usually, but not always, well known international companies or subsidiaries of multinational companies.

Sub-contract Enterprises

This group of companies varied in size from small organisations employing about 25 persons and only carrying out barrel zinc plating on a sub contract basis, to a large sub contract company employing 280 people and carrying out to a greater or lesser degree nearly all the electroplating processes used in metal finishing as well as the pretreatment processes necessary for satisfactory electroplating. In between are large enterprises carrying out specialised work in the engineering field such as hard chromium plating and electroless nickel plating, to a small enterprise specialising in the electroplating of plastics with nickel and chromium. What comes over in this series of visits is that by far the largest metal electrodeposited is zinc. The quality of work is uniformly high and nearly all companies have put in effluent treatment plant, are about to do so, or in some cases have been given permission to delay putting in new plant because they are about to move to a new factory. However, for a substantial number of firms the housekeeping is not as good as it should be and it will make meeting the new environmental requirements more difficult than it need be.

'In house' Enterprises

Generally the standard of housekeeping in the large and multinational companies is good and this is probably not surprising because there is a tendency in the multinationals to use the highest standard of safety and environmental welfare for employees from whichever country that standard is set. The companies visited were Olivetti, Degussa, Winter, and Gevisa, a jointly owned company of the General Electric Company of America and Veladis, a Brazilian Company.

The large companies in this group had nearly all installed their effluent plant some time ago. They were not strictly comparable to the smaller sub contract companies because they also had to consider that they used water treatment for other processes in their factories and not just for metal finishing. They were also, generally, large users of water with heavy water bills for the purchase and discharge of water. Consequently, they had made management studies of the consumption of water and had made substantial reductions in their consumption of water

Review Meetings

During the course of the six weeks, review meetings were held, in order to assess progress and make any changes of direction that might prove necessary The first of these was held at the SCTDE offices with Dr Klaus Billand, the Brazilian Director of UNIDO in Brazil being present . J K Cosslett reported on his activities so far and Dr Billand suggested that more non SINDISUPER firms should be visited.

A meeting was also held at the offices of FIESP, in the week before the end of J K Cosslett's visit. Present were Marco Barbieri of SINDISUPER, Dr Carlos Chanduri and Dr Robert Williams, both UNIDO staff members in Sao Paulo on another mission, Marli Ohiba, from IPT, Fernando Bartolla of SCTDE as well as David Brewer and J K Cosslett.

Mr Barbieri explained that CENTRAL SUPER was a group of 91 subcontract metal finishing firms who had banded together to set up an organisation to collect the filtercake that was the final product of the effluent treatment of metal finishing wastes. Other members of SINDISUPER who were not solely concerned with sub contract metal finishing were not in this consortium.

CENTRALSUPER were looking at a number of options including extracting the metals from the filtercake and incorporating the filtercake into the manufacture of cement. At present the interested parties in this project were IPT, SEBRAE, the Brazilian service for helping micro and middle sized enterprises, COPLASA, an offshoot of the international environmental company CH2 M HILL, SENAI, and IMT, a private university.

SEBRAE were putting into the project $1000 for every member of CENTRALSUPER. the members of CENTRALSUPER were putting in $300 each to a grand total of $118300, SENAI were contributing 80 man hours per CENRALSUPER firm , a total of 7280 man hours, for effluent treatment training in the Mario Amato school.

SEBRAE have also commissioned a feasibility study from IMT who have subcontracted this to COPLASA, who were due to report back by 8 October 1993.

On the penultimate day of J K Cosslett's visit a further meeting was held at the SCTDE offices in which representatives of SCTDE, SINDISUPER, David Brewer, Dr Billand and the project's backstop officer in Vienna, Dr Tamas Grof were present.

A verbal report on his activities was given by J K Cosslett on his findings and progress of the mission. Discussion followed and the main subject under discussion was the proposal to site the metal finishing firms on one site as a condominium. He had not come to any conclusion at that stage because he had not then translated the original proposal but his preliminary thoughts were that there was merit in the idea but that he could foresee practical and commercial difficulties.

II. OBSERVATIONS ON VISITS AND MEETINGS

Classifying the organisations by size was not straight forward because some large organisations had relatively small plating facilities, some companies which carried out heavy electrodeposition for engineering purposes would leave components in vats for a considerable length of time so that rinsing only represented a small part of the process, while other companies carried out barrel or vat plating on large numbers of components which were not in the plating vat for long periods and so the rinsing represented a large component of the process. In the case of one large company whose business was surface coatings for engineering purposes, electroplating only represented a part of the overall business the other part of the business was metal spraying which did not have a rinsing or effluent treatment element to it.

The overall impression as a result of visiting the limited number of the metal finishing firms in Sao Paulo was favourable for the following reasons:-

a) The quality of work seen was of a high standard.

b) In many, even small companies, the instrumentation used for inspection and quality control was comparable with that used in Europe,

c) Process control of solutions, either using their own laboratories, or using other company's facilities, was good and some organisations were using statistics for making the best use of that information.

d) The quality of technical management was generally good.

Where some of the firms seen were below standard was in housekeeping.

In those companies, the work areas were not as tidy as they should have been and floors were often broken and in poor condition. In some factories the work force appeared to be exposed to danger with unprotected machinery. For example, operators could get their fingers or hands trapped in exposed chains and cog wheels and operators did not have eye protection when they were using grinding wheels or polishing mops. Again chemicals were not stacked as neatly or as safely as they should have been.

This comparison is made with electroplating companies in Great Britain because this is where the writer has had the most experience. British electroplaters are not naturally more tidy than their Brazilian counterparts, but recent Health and Safety laws, which are strongly enforced, as well as the European legislation on the environment has forced changes in attitudes The new environmental regulations which are about to be enforced for discharge of effluent to the Rio Tiete will force the same changes that have occurred in Britain. These will be discussed more fully in the next chapter.

The results of these changes in laws in Britain has meant that great care has been applied to the layout of factories, storage areas and the avoidance of accidental spillage of chemicals to the drains. Consequently, everyday housekeeping has improved considerably. This is one of the results of enforcing this more stringent legislation.

A The Metals Deposited

Zinc

Zinc was by far the most common metal deposited in the enterprises seen. This was confirmed by reference to the information supplied by CETESB on the daily discharge to the Rio Tiete (Annex 3) and also information kindly supplied to J K Cosslett by two of the metal finishing supply houses Orwec Chemica S.A. and Anion Chemica Industrial Ltda based on their experience. There are implications for the proposals to recover metals from the filtercake or to put the filtercake into cement which will be discussed in the next chapter.

Chromium

Hexavalent chromium being discharged to sewers and water courses from the metal finishing industry comes from two sources,

(a) chromium passivation solutions which is used extensively in zinc and cadmium plating as a post plating treatment,

and

(b) from chromium trioxide, which is the basis of chromic acid plating baths for the electrodeposition of chromium both in decorative chromium plating, and in heavy chromium plating for engineering purposes.

Of the metals that are used in the metal finishing industry, this is the second most common metal found in the Rio Tiete according to the CETESB figures.

Copper

There are two main sources of copper discharge from the metal finishing industry, cyanide copper plating, which are alkaline solutions, and acid copper plating, usually from acid baths based on sulphuric acid. Coupled with this copper can be discharged from brass plating as, of course, can zinc. These are alkaline cyanide baths. However, there did not seem to be much brass plating in the enterprises visited.

Copper is the third most common metal normally deposited by the metal finishing industry to be found in the Rio Tiete.

Nickel

This is the fourth most common metal discharged to the Rio Tiete. In the metal finishing industry the two main sources of discharge are from

(a) electroplating baths

(b) electroless nickel baths which rely on autocatalytic reduction and deposition of nickel, usually in the form of a nickel phosphorus alloy.

Iron

In the CETESB list, iron is the second most common metal to be discharged to the Rio Tiete. Iron is not normally electrodeposited commercially in any great amount and of the enterprises visited, no iron plating baths were seen. However, in Sao Paulo there is a very large tonnage of steel components plated with zinc, and copper, nickel and chromium, as well as some cadmium.

The pretreatment of steel components prior to electroplating includes immersion in acids, usually sulphuric or hydrochloric acids, to remove iron oxides prior to the metal coating process. Obviously the iron salts go into solution which at the present find their way into the river.

Lead

The other major metal found in the Rio Tiete is lead. Whilst there is some electrodeposition of tin/lead solder alloy, it is difficult to see how this quantity of lead found in the river can come from the metal finishing industry. Very few of the firms visited carry out tin/lead alloy plating and none carried out just lead plating. Enquiries made locally of the plating industry and the supply houses confirm this.

Fluorides and Cyanides

The presence of cyanides in the river is to be expected because so many electroplating processes use metal cyanides. However, whilst some fluorides, for example hydrofluoric acid, are used in specialised pickling processes, and metal fluoborates are used in some electroplating processes, the figures quoted for fluorides quoted seem too high to come entirely from the metal finishing industry. Very few fluoride based processes were seen during the visits.

Tin

Although tin plating is carried out in Sao Paulo, it is not quoted in the list of materials discharged to the Rio Tiete.

Cadmium

The amount of cadmium plated in Sao Paulo is not very great and this is reflected in the low level of cadmium found in the river. However, cadmium is an extremely toxic metal and in Great Britain it is not now allowed to be discharged to the sewers or any water courses, a principal known as 'zero discharge'. Consequently, only those companies with the resources to instal the necessary equipment for treatment to remove cadmium completely from the effluent are continuing to offer cadmium plating as a service.

The remaining cations and anions

None of the remaining cations and anions quoted in the list are normally associated with the metal finishing industry, apart from boron when used as fluoroboric acid, and silver, which is a strong biocide and which should have been completely extracted for economic reasons.

B Effluent Treatment Plant

Of the metal finishing enterprises visited, only one appeared not to have made any plans to build an effluent treatment plant. One organisation, which carries out engineering coating and therefore has a relatively small effluent relative to the work done, collects the rinses for treatment in another factory in the same group. Another three companies are in the process of moving to new sites where they are constructing effluent treatment plant in anticipation of their move. They have received permission to delay implementation of the new regulations due to start on 1 October 1993 until they move to their new sites within the next few months.

All the remaining enterprises had just built, or were just completing, the construction of their effluent plant. They are all building the conventional effluent treatment plant, namely, sodium metabisulphite treatment of hexavalent chromium in acid solution, hypochlorite treatment of cyanide in alkaline solution, then blending the treated rinse waters with the ordinary acid and alkaline rinses, adjusting the pH to 8.5 to precipitate the metal hydroxides, allowing to settle and then pumping the resulting hydroxide sludge through a filter press to form a filtercake which will contain about 40% moisture.

One of the major subcontracting companies which is shortly to be moving to a new factory, has in addition to putting in the conventional effluent treatment plant on the new site, will also be evaporating rinse water from the chrome plating rinses to return the concentrate to the plating bath. The company will also be putting in ion exchange resins on the rinse lines of its nickel plating processes and copper plating processes in order to trap the nickel and copper for reuse in other processes.

C Water Consumption

Again, with the exception of one company, all companies seem to be addressing the question of water consumption, and they are combining the building of new effluent plant and looking at their processes to identify ways of reducing water consumption. This means, that as most of the companies would start running their new effluent treatment plant within a matter of weeks of these visits, present water consumption figures might have little relevance for the future.

Nonetheless, some figures are given for guidance:-

a) a small subcontract company employing 26 people and only carrying out barrel zinc plating and chrome passivating uses 30 m^3 of water per day.

b) A company making specialist nuts and bolts, has its own captive plating shop which employs 17 people and uses 14m^3 of water per day barrel zinc plating followed by passivation of its own products.

c) At the other end of the scale, the total consumption of water for all processes at Olivetti is 350m^3 per day. It is interesting to note in passing that they reduced their water consumption from 1100 m^3 per day and in doing so reduced their water bill saving $800 000 in 1992 and reducing the estimate for their effluent plant from $5 000 000 to $500 000 in the process!

d) Another zinc plating enterprise, this time a mixture of barrel plating and vat plating of zinc, employing 35 people. They zinc plate 300 tons of components a month, use 30m^3 of water per day and operate for 24 hours a day.

e) Gevisa S A, in the town of Campinas, have a small plating shop which electrodeposits silver, tin, and zinc on to copper and steel components. This plating shop consumes 30m^3 of water per day in an 8 hour working day but they are looking at methods for reducing their consumption of water by such techniques as vacuum evaporating rinses to recycle the clean water and returning the concentrate to the plating baths. At present they have their own ground water for which they make no payment, but pay $3 m^{-3} to discharge water. In the future they will have to pay to abstract the ground water. Incidentally, this is the first Company in South America to be awarded ISO 9000.

CETESB and SABESP

The inter relationship between CETESB and SABESP is that CETESB have a supervisory role on environmental matters concerning discharge to rivers very similar to the system in Great Britain where the National Rivers Authority has a supervisory role on discharge to rivers. In this sense CETESB can apply sanctions to SABESP. In Great Britain the National Rivers Authority can prosecute the water companies for breaking pollution limits in discharge to rivers and estuaries.

SABESP do not monitor industrial effluent discharges. This is done by CETESB who sample and analyse from the factory outflow. SABESP do not have an accurate measure of the water usage because 34% of the water that they supply is subsequently unaccounted for. SABESP would like CETESB to control the discharge of metals into the sewage system. They would also like CETESB to apply regulation 18 rigorously.

Sanctions that apply to enterprises that do not meet the discharge limits is a tax that is doubled every month until the limits are met.

Water is supplied to enterprises at an average price of $2 m^{-3}.

III. DISCUSSION

Because of the deadline set on implementation of the regulations for discharge to the Rio Tiete, most of the energetic and forward looking companies had already built their effluent treatment plant by the time the writer arrived in Sao Paulo. No doubt, because time was short, all companies that had completed, or were close to completion, installed the standard process of hypochlorite treatment of cyanides, sodium metabisulphite reduction of hexavalent chromium to trivalent chromium, then merging all the water discharge lines, adjusting the pH to 8.5 precipitating the metal hydroxides, allowing them to settle and filtering through a filterpress to produce a filtercake of about 40% moisture content. With one exception, no one installed alternative means of recovery for chemicals and metals such as electrolytic recovery or ion exchange David Brewer, the water treatment expert will comment separately on the detail of water treatment plants being installed.

CETESB are only interested in the discharge limits to the Rio Tiete being met. How this is done is up to the metal finishing industry. This has left the metal finishing industry in Sao Paulo with the problem of dealing with the sludge Again, CETESB will not allow the metal finishing industry to put the sludge and filtercake into landfill within the limits of the metropolitan area of Sao Paulo. It has to be said that there seems to be some confusion on this point. CETESB told Brewer and Cosslett , that if the metal finishing industry found suitable sites in the state of Sao Paulo, they could use them, but that the metal finishing would have to bear the cost. However, Brewer and Cosslett formed the strong impression that the metal finishing industry did not think that they would be allowed to use landfill sites

This has left the industry with some difficulties. The Sao Paulo metal finishing industry did not seem to explore all the options that were available for effluent treatment and recovery Consequently, the local metal finishing firms made their capital investments, and some of the suggestions that were made by J K Cosslett at his presentation on 28 September to SINDISUPER will cause the individual firms extra expense if they decide to take them up.

It would have been better if UNIDO had become involved with these problems at least 18 months earlier.

A Centralized treatment of Waste, Metal Recovery and Condominiums

The main consideration of the supervising authorities is the reduction or elimination of contamination of the Rio Tiete The main considerations of the metal finishing industry are that the effluent discharge conforms to the limits set by CETESB, and the disposal of the filtercake or extraction of metals from the filtercake that is produced by the effluent treatment process.

Those metal finishing organisations which are purely subcontractors have set up a separate organisation called CENTRALSUPER. The idea is to bring the filtercake to one central clearing point from where it will either be sent to the state of Parana for incorporation into the manufacture of cement, or means will be devised to extract the constituent metals.

Both of these ideas are untested, as far as is known, anywhere in the World. David Brewer asked contacts in the UK to make enquiries and he received the reply that such metals as zinc, copper, nickel and tin must not exceed 0.1 to 0.2% in total otherwise the strength of the cement is impaired, and furthermore even lower quantities may impair air quality coming off the kiln. Zinc oxide sublimes appreciably above 1400°C.

It has been mentioned earlier in this report that the most common metal electrodeposited in Sao Paulo is zinc and this is certainly born out by reference to the analysis figures supplied by CETESB (ANNEX III) of contaminating metals in the Rio Tiete. It follows that the most common metal in any filtercake produced from the effluent treatment will be zinc. Zinc is not a particularly expensive metal and a question has to be asked whether it is economically justifiable to extract zinc from the filtercake by extractive metallurgy. A number of the subcontract platers only carry out zinc plating and chromate passivation, which means that the separation of two metals should be easier than if there are many metal hydroxides present. However some platers carry out a number of electroplating and other processes so that the separation of the metals is going to be even more difficult. During the course of the last meeting Dr T Grof referred to Hungarian work in which a flow sheet was developed for the separation of mixed metal compounds and this could be worth pursuing.

Two of the companies visited, Winter and Gevisa, are looking at the possibility of sending their solid residue to the USA for processing. The companies would have to pay for transporting the solid residue to the USA and also for its treatment. Gevisa gave tentative figures of $250 a ton for treatment and $150 ton for transport. The treatment costs would be determined by the analysis of the solid residue because presumably some of the costs for the processor would be offset by selling treated material onwards. Presumably these two companies anticipate that this will be cheaper than sending it to CENTRALSUPER. These two companies cannot join CENTRALSUPER because they are not subcontractors, but presumably they could pay to use the CENTRALSUPER facilities if they wanted to. Gevisa electrodeposit silver, tin and zinc on to copper or steel. Winter deposit nickel and bronze.

It would be desirable if the metal finishing companies could separate their rinse lines and treat the metals separately. This obviously means extra expense in the short term but having to deal with the salts or hydroxides of single metals is clearly an easier option. This does lead on to two methods that

could be added to the existing systems which, if linked to more efficient rinsing , would enhance the conventional effluent treatment plant that has already been installed.

In the chapter entitled 'Recommendations', a number of suggestions in plating shop practice have been made and will not be repeated here. However, one of them, counter current rinsing, can be used to illustrate improved rinsing combined with a reduction in the use of water. Let us suppose we have a plating tank with 20 000mg/l of cyanide, and work is rinsed in a single rinse tank flowing at 100 litres per hour. If we dragout from the plating tank at 0.2 litres per hour, then at equilibrium the average dilution is (100/0.2)=500

Therefore, the concentration of cyanide in the rinse is (20 000/500)mg/l = 40mg/l (or 40ppm)

If we use the same dragout and the same flow rate of rinse, but this time use two tanks in cascade flowing counter to the direction of the flow of work, then the concentration of cyanide in the first tank is, again 40mg/l but in the second rinse (the first one in the flowing sequence) then the concentration of the cyanide is (40/500)mg/l=0.08mg/l.

What is required is improved rinsing and improved water consumption. Using a two stage rinse flowing at 20 litres per hour and still dragging out 0.2 l per hour of plating solution then in the first rinse the dilution will be (20/0.2)=100 so the concentration of cyanide in the first rinse will be

(20 000/100)mg/l=200mg/l

and in the second rinse will be (200/100)mg/l=2.0mg/l

Thus comparing the very first situation with the last situation we have an improvement of rinsing efficiency of 20 times and a reduction of water consumption to a fifth of the original use.

Now combining improved rinsing and reduced water consumption with two methods of metal recovery there is scope for achieving reduced contaminated discharge to the Rio Tiete, as well as returning metals into the plating sequence. The two methods that are established and will be considered here and are commercially available are Electrolytic Recovery and Ion Exchange

Electrolytic Recovery

This works on exactly the same principle as electroplating except that the concentration of contaminants in dragouts and rinses is much more dilute. To overcome the polarisation problem and the very slow plating rate that would normally take place, chemical engineers have devised a method of breaking up the boundary on the electrode surface by fluidising very small glass or ceramic balls, called ballotini, in the solution to be treated. Electrodes are placed in the solution and electrolysis proceeds

until the metal to be recovered is reduced in the dragout to a very low level suitable for discharge. The metal is recovered on the cathode, usually in a very pure state, and can either be used, in certain circumstances, as an anode in the original plating bath or stripped off the cathode and sold for high quality scrap.

This is called a CHEMELEC cell and was invented and patented by the Electricity Council of Great Britain who licensed it world wide to a British company called BEWT.

Ideally, the cell should be used for one metal at a time. It can be used with all the precious metals as well as nickel, copper, tin, bronze, zinc, lead, and electroless nickel. It is not suitable for iron, chromium and aluminium.

It is claimed that

a) cells can recover metals to less than 1ppm (1mg/l)in the water to be discharged,

b) cyanide is totally destroyed at the anode,

c) it solves the biological oxygen and chemical oxygen demand problem

d) many complexes, for example EDTA, are broken down at the anode.

The very low levels claimed for discharge are achieved after prolonged electrolysis.

These cells are not cheap . A small cell recovering 0.5 to 1.0 kg per week costs $6000, a cell recovering 3 to 5 kg per week cost $12750 to $15000, and larger cells cost more.

This cell works well in combination with other processes. Dragouts can be electroplated down to an acceptable level then the dragout can be passed through an ion exchange column to remove the balance of the metal. This speeds the up the process and prolongs the life of an ion exchange column before it needs regeneration. The electrolytic method works well in combination with the conventional plant reducing the metal content to the effluent plant making it easier to meet discharge limits.

Ion Exchange

The principle of this method is that special resins with an active centre will exchange a hydrogen ion with the metal to be extracted or in the cases of an anion exchanger the anion radical to be trapped is exchanged for an acceptable anion radical such as chloride

When the resin cartridge is saturated it is replaced with a fresh cartridge while the metal can be extracted from the used cartridge by elution with a suitable acid or salt. Each cartridge should be kept for use with one metal or anion only.

This now opens up the possibility of taking advantage of the desire in Sao Paulo to have a central treatment area. The following suggestion was in a data sheet of one of the ion exchange resin suppliers, Rohm and Haas. When a cartridge is saturated with the ions of the metal that is being collected it can be taken to a central treatment point where it can be eluted into a tank allocated for a particular chemical, for example, nickel chloride. This will now be in a much more useful concentrated form. The plating company will of course have a spare cartridge to put in the rinsing line. In this way, all plating companies can have their nickel wastes treated, their copper wastes treated, and so on. CENTRALSUPER could be the focus for this system. They could own the system, and hire out the cartridges to their members. The concentrated salts can be returned to the plating processes or sent on for further processing in any way that may be required.

Condominiums

A paper entitled ' Distrito Industrial Para Pequenas e Medias Industrias Poluidas: Proposta Preliminar' was published by the Secretaria Da Estado Do Meia Ambiente Coordenadoria Do Planejamento Ambiental of the State Government of Sao Paulo in May 1990. In this it was proposed that similar industries should be grouped together on the same sites as specialist industrial estates. In this way the metal finishing industry would be grouped together and could share common utilities such as water and electricity supply and have common treatment of liquid effluent and atmospheric contamination.

This is a very new idea in which the writer has no experience so would not wish to give a judgement one way or another without seeing a detailed analysis of how it is proposed to apportion costs for treatment of the effluent in proportion to discharge of contaminants by individual firms. Another area that would need further study would be the question of transport of goods to and from the customers of the subcontract metal finishers. The metal finishing industry is a service industry to the manufacturing industry and, traditionally, is usually sited within relatively easy reach of its customers. The traffic congestion in Sao Paulo is extremely bad and the effect of this on the transportation of goods to be sent to a condominium that may not be within easy reach of the manufacturing base, should be included in any detailed study of the plan.

The writer has not seen the Coplasa/IMT proposals on sludge treatment and disposal so cannot comment on them. Should they become available at a later stage he is prepared to add comments as a supplement to this report.

Conclusions

The technical management in the metal finishing industry is generally of a high order as has been demonstrated in the areas of quality control and process control so that there is no doubt that the intellectual ability to deal with these environmental problems is available. Nonetheless, the housekeeping in a number of the plating enterprises seen is not as good as it should and will need to be improved if the industry as a whole is to meet the new discharge limits to the Rio Tiete.

The industry generally, has opted for the classical treatment of metal finishing effluent treatment and it is not separating its rinsing lines. The result is that it will have a filtercake of mixed metal hydroxides to deal with, for which there is no easy treatment available.

There are two technical institutions seen by the writer which complement each other and can be used to the full by the metal finishing industry in Sao Paulo. They are the metal finishing school at the SENAI School Mario Amato under Mr Cesta, and the Corrosion and Metal Finishing Department of the IPT under Dr Panossian. In discussion with Dr Panossian, the writer asked her if her department could play a role in the development of the treatment of metal finishing sludge. She explained that they had no experience in this particular area of the industry and that there would be a learning curve if they were to be involved. However, they would be prepared to become involved as it would widen their input into the metal finishing industry

RECOMMENDATIONS

Some of the comments made earlier in this report on the state of metal finishing industry in Sao Paulo have already been made to SINDISUPER on 28 September 1993. Some of the practical comments and suggestions that are to follow were also made at that presentation. These comments are mainly aimed at reducing water consumption which is something that can be done now with relatively little extra expense and in fairness, some of the enterprises are doing this already.

A Plating Shop Practice

Determination of Optimum drainage Rates

The faster a work piece is withdrawn from a solution the thicker the liquid film on the surface. If this is not allowed to drain thoroughly, the dragout of solution from the process bath becomes excessive and eventually finishes up in the effluent treatment plant. The drainage rate for a component or barrel load of components can be made by simply measuring the drainings into a container and measuring the volume collected. In this way a balance can be struck between the amount of time to be allowed for drainage and the speed of production.

Personnel Training

Shop floor personnel to be trained in good plating shop practice at the SENAI School Mario Amato under the direction of Mr José Francisco Cesta. It is also recommended that this school should run refresher courses for management.

Process Control

Most plating materials supply houses give operating ranges for their processes. By regular analysis it is possible to operate processes at the lower end of their operating range, thus reducing dragout losses.

Spray Rinsing

Where it can be applied, the use of spray rinses over heated process tanks washes dragout back into the process solution

Spray rinsing, generally, is the most efficient method of rinsing and thus the volume of rinse water can be kept to a minimum.

Drip Trays

These are trays that are placed between the process tank and the first rinse or dragout, so that drips from the work being processed can be collected and returned to the process solution.

Dragout Baths

These are important and are used to collect the first rinse from the process solution. They are static baths which do not run to waste. When the contaminant builds up, if the process bath runs at an elevated temperature, the dragout can be returned to the process to replace the evaporation losses in the process tank. In some cases it might be useful to have a second dragout bath. When the first dragout becomes too concentrated and is sent for recovery, the second bath can be made the first and a new second bath made up.

Counter Flow Rinsing

By running two or more rinse tanks in the opposite direction to the flow of work so that the work is rinsed in the last bath of the cascade first and is then rinsed in the baths in the cascade in sequence to the first bath in the cascade. very efficient rinsing can be achieved with the economical use of water.

Forced Air Rinsing

By blowing clean, oil free air through the rinse water, very efficient rinsing can be achieved.

Flow Restriction

By fitting flow restriction valves to the water supply to rinse tanks, which cannot be tampered with by staff, good economies can be achieved. It is necessary to determine beforehand the optimum rinsing conditions for that particular process.

Conductivity Meters

A conductivity meter in the final running rinse of a process, setting it to a predetermined conductivity, it can be made to control a solenoid valve in the water supply to the rinse. When the conductivity of the rinse is too high, the valve lets water in, when the conductivity of the water falls to a predetermined level it switches the water off. Care must be taken not too set the conductivity level too low or water will be wasted.

Lunch Breaks

Switch off the water during lunch breaks.

General Maintenance.

Check all pipework and tanks for leaks and repair any faults immediately.

Inspect plating barrels and plating jigs regularly. Barreis with blocked holes trap process solutions, Jigs that have excessive build up cannot function properly and cause substandard and rejected work.

Quality Control

Reducing the reject rate reduces the need for stripping and replating. This reduces the metal build up in the stripping solutions and reduces the need to put components through the plating process too many times and thus reduces losses through dragout.

B Waste Management. Centralised Treatment and Condominiums

1) Individual companies should look at separating their rinse lines to simplify waste treatment to try to recover metals individually.

2) In addition to their present proposals for the central treatment of filter cake, CENTRALSUPER could explore in some detail the use of ion exchange in the treatment of rinses in order to produce single solutions of plating metal salts and possibly come to a commercial arrangement with that member of their group which is using this system, to share its experience.

3) Individual firms and SINDISUPER to explore further the use of electroytic recovery of metals and how any capital investment should be funded should it prove to be a viable option for Sao Paulo.

4) It will be necessary for there to be detailed knowledge of the effluent from individual firms. CETESB will have that knowledge and should make it available to the individual firms so that they can plan the their treatments in more detail.

5) IPT should be asked to advise on more theoretical aspects if there is any development work to be carried out.

6) UNIDO should make available such information it may have on the metallurgical extraction of metals from filtercake.

7) SCTDE to explore in more detail the commercial implications of the Condominium proposal from the following aspects:-

a) how it is going to apportion effluent treatment charges in proportion to the use individual firms make of the treatment, and

b) what effect will putting the metal finishing firms together on one site have on the logistics of transporting goods to be finished from manufacturers to finishers and back again, given the severe traffic problems in Sao Paulo.

With respect to 7(a), SCTDE will need to have accurate measurement of flow of effluent from each individual company and accurate analysis of the effluent in order to calculate the consumption of treatment chemicals used by each individual company.

8) J K Cosslett to look at and comment upon the Coplasa/IMT plan and issue a supplementary report if the plan becomes available within a reasonable time.

ANNEX I

JOB DESCRIPTION

SI/BRA/93/801/11-01/J13102

Post Title: Expert for electroplating, galvanizing and surface treatment of metals.

Purpose of project: The project aims at advising the Government of the State of Sao Paulo how to contribute to the reduction of the severe pollution of the Rio Tiete in the metal treatment (electroplating) industry.

Duties:

1) Survey of selected electroplating and surface finishing industries.

2) Classification of enterprises by size, types of technologies and nature of the solid and liquid waste discharge.

3) Preparation of recommendations on improvement of technologies through relatively low investments and simple technology modifications with the aim of reducing consumption of chemicals and metals and discharge of pollutants.

4) Preparation of recommendations for the in situ treatment of waste streams and recycling of heavy metals and chemicals.

5) Recommendations on collection of different types of waste for centralized treatment , recycling of heavy metals and chemicals for the safe disposal of residues.

6) Recommendations for the establishment of centralized treatment, recycling plant for sludges and other wastes of the metal surface finishing. Advice on cooperation between the plants to treat waste of several plants in the existing treatment facilities on a toll basis.

7) Recommendations on the criteria for relocation of metal surfaces finishing plants to a specialized industrial estate and selection of enterprises to be located.

8) Preparation of guidelines for the infrastructure of the industrial estate designated for metal surface finishing including disposal etc.

ANNEX II

Names of Brazilian participants in the project:-

Roberto Usberti - SCTDE

Fernando Batolla - SCTDE

Sergio Dimitruk - SCTDE

Dr Zehbour Panossian - SINDISUPER and IPT and interpreter

Ms Marli Ohba - main interpreter and IPT

Francisco di Giorgi - IPT and interpreter

Marco Barbieri - SINDISUPER and CENTRALSUPER

Dr Fernando Craveiro de Sa - SINDISUPER

Ms Carmen Silvia de Lima -SINDISUPER and CENTRALSUPER

Others who were prominent during the project:-

Volkmar D Ett, FIMF - International Union of Metal Finishing

Marco Antonio de Paiva Vital -SINDISUPER

Sergio Evangelista - SINDISUPER

Sergio Roberto Andretta - SINDISUPER

Glossary of abbreviations

SCTDE = Secretaria da Cienca, Tecnologia e Desensolvimento Economico

SINDISUPER = Sindicato da Industria de Protecao, Tratamento e Transformacao de Superficies do Estado de Sao Paulo.

IPT= Instituto de Pesquisas Tecnologicas, the Institute of Technological Research

SABRAE= The Brazilian Service for helping Micro and Middle Enterprise.

FIESP = Federacao das Industrias do Estado de Sao Paulo

CENTRALSUPER= The 'sub contractors only' members of SINDISUPER.

CETESB= The environmental agency of the Government of the State of Sao Paulo

SABESP= The water supply and treatment organisation of the State of Sao Paulo

ANNEX III

The discharge analysis of metals and anions to Rio Tinto on a daily basis

Metal or anion	kg/day
Chromium	344,88
Cyanide	123,5
Copper	257,03
Lead	141,12
Iron	477,11
Mercury	0,31
Nickel	228,64
Fluoride	280,94
Barium	2,75
Arsenic	0,04
Boron	18,95
Cadmium	2,58
Silver	1,89
Zinc	982,38

ANNEX IV

The following is a summary of the points applying to metal and anion discharge to rivers and sewers as they affect the metal finishing industry

NOTE:- article 18 represents State discharge limits to rivers, article 21 are Federal limits of discharge to the rivers and article 19-A State regulations on discharge to sewage works.

Parameter	units	art 18	art 21	art 19-A
Lead	mg/l	0,5	0,5	1,5
Cyanide	mg/l	0,2	0,2	0,2
Copper	mg/l	1,0	1,0	0,2
Cr^{6+}	mg/l	0,1	0,5	1,5
Cr^{3+}	mg/l	-	2,0	-
Cr total	mg/l	5,0	-	5,0
Tin	mg/l	4,0	4,0	4,0
Soluble Fe	mg/l	15,0	15,0	15,0
Fluorides	mg/l	10,0	10,0	10,0
Soluble Mn	mg/l	1,0	1,0	-
Mercury	mg/l	0.01	0,01	1.5
Nickel	mg/l	2,0	2,0	2,0
Silver	mg/l	0,02	0,1	1,5
pH	pH units	>=5,0 to=<9.0	>=5,0 to=<9.0	>=6,0 to=<10.0
Temperature	°C	<40	<40	<40
Cadmium	mg/l	0,2	0,2	1,5
Sulphate	mg/l	-	-	1000,0
Sulphide	mg/l	-	1,0	-
Sulphite	mg/l	-	1,0	-
Zinc	mg/l	5,0	5,0	5,0