ENVIRONMENTAL ASPECTS AND USE OF "CLEAN TECHNOLOGIES" FOR SURFACE FINISHING INDUSTRIES IN FRANCE

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1. CETIM : PRESENTATION

CETIM is the technical center for mechanical engineering companies which was created in 1965 by and for the mechanical industry to help the industrials to be more competitive.

CETIM's main function is to place the results of its work and available technologies at the disposal of mechanical engineering companies.

CETIM can propose to mechanical engineering companies a wide range of technical services ; such as tests, measurements, inspections, advice, specific studies as well as training and technological information through periodicals, books and softwares.

CETIM is run by the mechanical industry and under government control. In 1993, the budget was 340 MF(~57M US$) excluding the value added tax(VAT : 20.6%).

CETIM is financed through 3 main sources :

- 67% comes form a tax on mechanical industries which are registered with CETIM(0.1% of their sales)
- 25% from services that CETIM provide
- 8% from public and other contracts.

Today CETIM employs on three sites in

France, 630 people of which :

- 290 engineers and executives,
- 190 technicians,
- 150 manual and office workers.

2. SURFACE FINISHING INDUSTRY IN FRANCE

There is two kinds of companies in this industry :

- Surface finishing workshops : for which surface finishing is the main activity,
- "Joined" Surface finishing companies : for which surface finishing is only a step of a production process.

The total turn-over of surface finishing activity is 32000MF(~5.3 billions US$) of which 12000MF(~2billions US$) is made by workshops. The main figures describing workshops' activity are :

50% of workshops are 20-people or less workshops,

20% of the 20,000 people working for workshops are working for workshops of 20-people or less,

20% of workshops' turn-over is made by workshops of 20-people or less,

30% of the national turn-over for workshops of more than 20-people is made with electroplatings or electroless coatings,

27% of the national turn-over for workshops of more than 20-people is made with organic coatings,

11% of the national turn-over for workshops of more than 20-people is made with hot-dip galvanizing.

These figures show that surface finishing activity in France is mostly done by small and specialized units.

3. ENVIRONMENTAL REGULATION IN SURFACE FINISHING INDUSTRY

As surface finishing activity uses hazardous substances to health, the French activity is placed under a specific regulation(September 26th, 1985 Decree). This regulation considers :

- use of "good practices"(frequency of analysis, data's' recording, overflow protection tanks, closed-loop cooler systems, level gauges', ···)
- maximum limits of pollutants in water and air(Tab. 1, Tab. 2),
- Water consumption limits(Tab. 3),.
- maximum limits of pollutants released by solid wastes(Tab. 4).

Tab. 1

Water limits	
Pollutants	Limits
Chromium(VI)	0,1mg/l
Chromium(III)	3mg/l
Cadmium	0,2mg/l(*)
Nickel	5mg/l
Copper	2mg/l
Zinc	5mg/l
Iron	5mg/l
Aluminum	5mg/l
Lead	1mg/l
Tin	2mg/l
Solids	30mg/l
Cyanides	0,1mg/l
Fluorides	15mg/l
Nitrites	1mg/l
Phosphorus	10mg/l
Total hydrocarbon	5mg/l
COD	150mg/l

Tab. 2

Air limits	
Pollutants	Limits
Total acidity(H^+)	0,5mg/Nm^3
HF(Fluoride)	5mg/Nm^3
Total Chromium	1mg/Nm^3
Chromium(VI)(if bath>50m^3)	0,1mg/Nm^3
Cyanides	1mg/Nm^3
Alkalinity(OH^-)	10mg/Nm^3
NOx(NO_2)	100ppm

Tab. 3

Water consumption per rinse function
<8 liters per m^{-2} coated

Tab. 4

Leaching test limits on solid waste	
Pollutants	Limits
pH	between 4 and 13
Dryness	>35%
Solubility	<10%
COD	2000mg/kg
Phenolics	100mg/kg
Chromium(VI)	5mg/kg
Total chromium	50mg/kg
Lead	50mg/kg
Zinc	250mg/kg
Cadmium	25mg/kg
Cyanides	5mg/kg
Nickel	50mg/kg
Arsenic	10mg/kg
Mercury	5mg/kg

This national regulation is the minimum requirement. At anytime, a local regulation can be added to tighten the national one. This re-enforcement even can go to the zero-liquid discharge!

The main parameters of the national regulation are showed in the Tab. 1, 2, 3, 4.

4. "CLEAN" TECHNOLOGIES, BEST TECHNOLOGIES AVAILABLE(BTA)

The following case studies where conducted by CETIM in order to give to surface finishing industrials the information needed to choose technologies able to reduce waste and pollution in several processes of surface finishing.

These tests were run on industrial sites, under industrial conditions and using equipment available on the French or European market.

Case 1 : Alkaline degreasing bath

Technical aspects :

A workshop of 5 people specialized in barrel zinc electroplating(cyanide) for the car industry used to have trouble with COD in his treatment plant. CETIM proposed to connect a skimmer to one of his degreasing baths(Fig. 1)

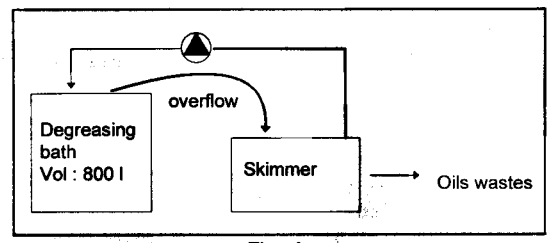

Fig. 1.

The results of COD analysis on the degreasing bath with or without skimmer(Fig. 2 and 3) shows that the equipment can be adapted to the pollution normally observed in degreasing baths(oils, greases, ···).

Economical aspects :

The economical study shows that the equipment is acceptable for the industrial situation.

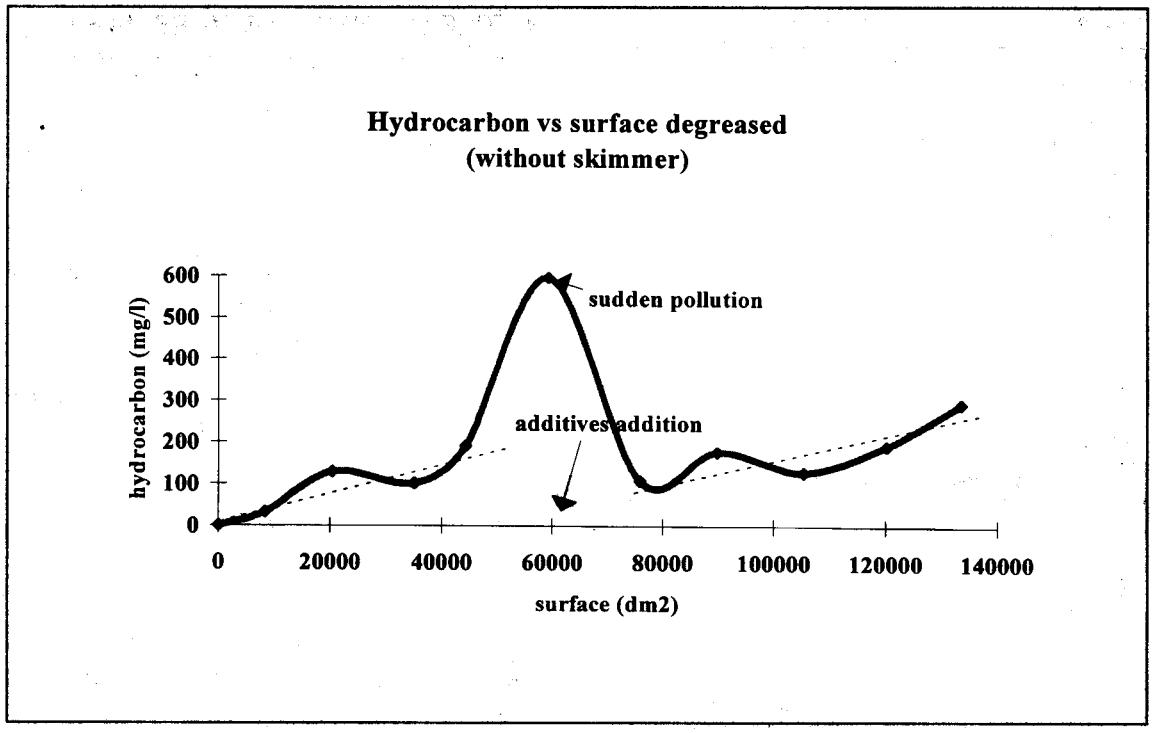
Hydrocarbon vs surface degreased
(without skimmer)
hydrocarbon (mg/l)
600
500
400
300
200
100
0
sudden pollution
additives addition
0
20000
40000
60000
80000
100000
120000
140000
surface (dm2)

Fig. 2.

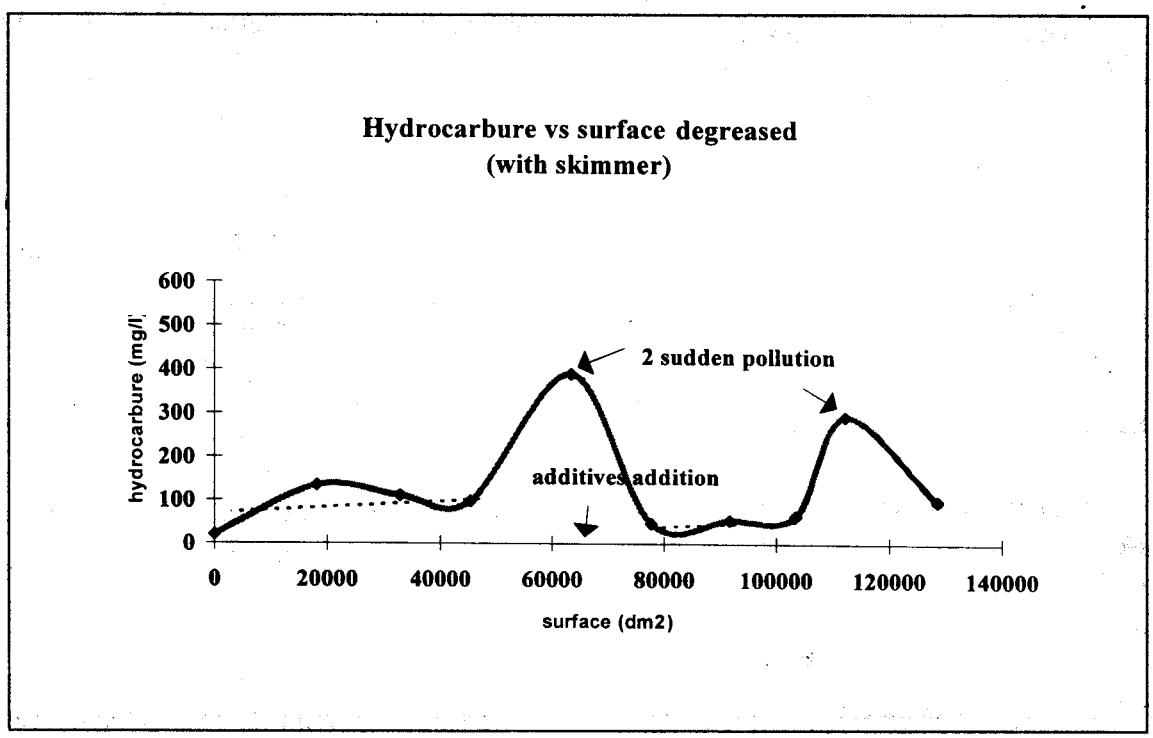
Hydrocarbure vs surface degreased
(with skimmer)
hydrocarbure (mg/l)
600
500
400
300
200
100
0
2 sudden pollution
additives addition
0
20000
40000
60000
80000
100000
120000
140000
surface (dm2)

Fig. 3.

Costs involved	Without skimmer (4 treatments every 2 months)		With skimmer (1 treatments every 2 months)	
Baths destruction	1,800	(3200l)	450	(800l)
Baths costs	1,400		350	
Additional compounds	700	(60kg)	525	(45kg)
Oils wastes destruction	0		35	(75l)
Electricity	0		135	
Maintenance	200	(2h)	50	(30mn)
TOTAL(Francs)	4,100		1,525	

skimmer cost : 37,975F.HT ➡ Return on cost : 2,5years

Case 2 : Nickel Watt rinse and bath

Technical aspects :

A workshop of 8 people specialized in nickel Watt coatings(jigs) for eye-glass frame industry used to have trouble with nickel limits in his effluents treatment plant. CETIM proposed to connect an electrodialysis(ED) equipment to both nickel bath and following rinse.(Fig. 4)

To optimize the ED treatment(to avoid clogged or polarized membranes), it was decided to switch the polarity every 3 hours.

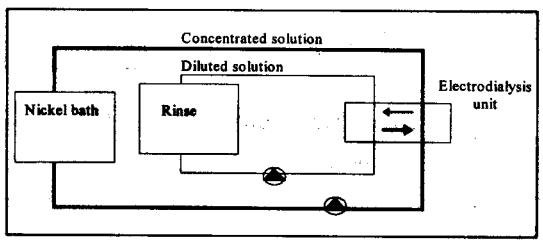

Fig. 4

The result of the nickel, chloride and sulfate analysis on both bath and rinse(Fig. 5 and Fig. 6) was technically satisfactory ; the main remarks were :

- the bath is regenerated(Tab. 1),
- as the rinse treated stays clean it is possible to reduce following rinses flow rates,
- reduction of sludges,
- increasing process control,

the concentrated solution needs to be treated by H202 and filtration to avoid rising of additives concentration.

Tab. 1.

	Concentrated solution composition(after 240mn)	Nickel bath composition
$[Ni^{2+}](g/l)$	47,2	54,3
$[SO_4^{2-}](g/l)$	48,3	53,0
$[Cl^-](g/l)$	38,7	26,7

The economical study shows that the equipment is not suitable for the industrial situation.

Economical aspects :

Estimated nickel pollution to be treated : 320kg per year

equivalent in hydroxides sludges : 3200kg per year

Costs involved	Without ED unit	With ED unit
- Chemicals use in the treatment plant(NaOH, H_2SO_4,…)	960	~0
- Sludges dumping	4800	~0
- Electricity	0	600(1200kWh/year)
- Maintenance	0	2000 (100h/year)
- Others (filters, membranes, …)	0	5000
- Water savings	0	-3050 ($380m^3$/year)
- Nickel salts savings ($Sulfate^-$: 1150kg, Chloride : 225kg)	0	-21500
TOTAL(Francs)	5,760	-16,950

ED unit cost : 250,000F ➡ Return on cost : >10years

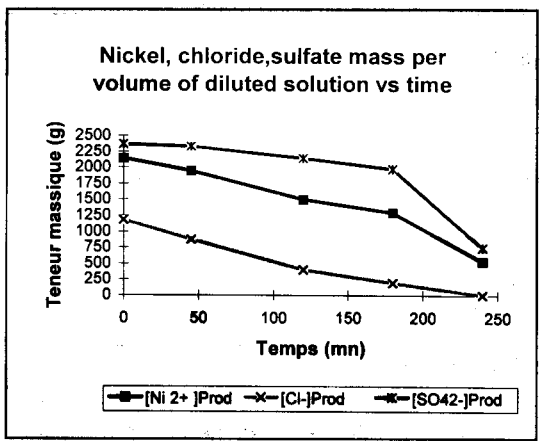

Fig. 5

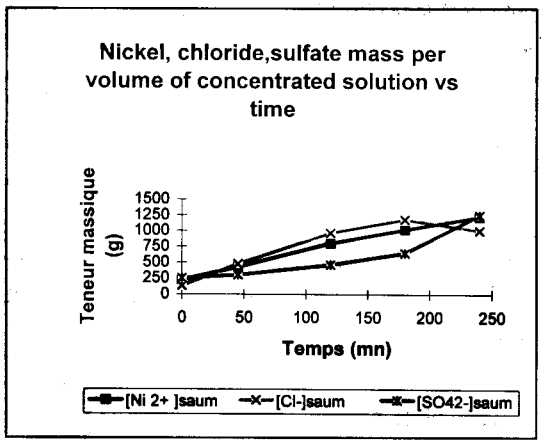

Fig. 6

Case 3 : Hard chromium bath

Technical aspects :

A workshop of 30 people specialized in hard chromium coatings used to have trouble with hard chromium bath polluted with iron. CETIM proposed to use an ion exchange unit(ECOTEC system) to treat the hard chromium bath in order to remove iron.(Fig. 7.)

The result of the hexavalent chromium, iron and sulfate analysis on hard chromium bath(Tab. 2.) was technically satisfactory ; the main remarks were :

- a solution of diluted bath is regenerated (regenerated solution volume/treated hard chromium bath volume=2),
- reduction of hazardous waste,
- increasing process control by iron concentration control,
- no negative impact on hard chromium coat,
- large volume of sulfate wastes generated (waste volume/treated hard chromium bath volume=6)

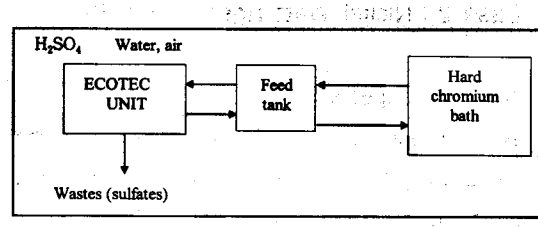

Fig. 7

Tab. 2.

	Hard chromium bath	Feed tank	waste
CrO_3(g/l)	188.0	118.4	0.93
SO_4^{2-}(g/l)	2.9	1.87	41.2
Fe^{3+}(g/l)	11.7	0.14	2.35
Cr^{3+}(g/l)	5.6	<0.1	1.2
Ratio(CrVI/sulfate)	65	63	

The economical study shows that the equipment is only suitable for the industrial situation if there is not an effluent treatment plant or the use of an another technology to reduce the sulfate waste volume.

Economical aspects :

Solution 1 : The industrial uses external services to treat his hard chromium bath when polluted with iron(normal use for hard chromium activity)

Solution 2 : The industrial has his own treatment plant and uses an ion exchange unit

Costs	Solution 1(kF)	Solution 2(kF)	Solution 3(kF)	Solution 4(kF)
hard chromium baths haulings and destruction ($20m^3$, 38t)	86	0	0	0
Baths costs	100	0	0	0
destruction maintenance	10	0	0	0
Ion exchange unit cost return (4 years)	0	50	50	50
Ion exchange unit maintenance and electricity	0	40	40	40
Sulfate wastes haulings and destruction ($10m^3$/month)($1m^3$/month with evaporator)	0	0	180	17
Storage tank	0	0	5	5
Effluents treatment plant	0	12	0	0
Solid wastes(20t)	0	30	0	0
Evaporator cost return(4 years)	0	0	0	100
Evapoator maintenance and electricity	0	0	0	30
TOTAL	196	132	275	242

Solution 3 : The industrial uses an ion exchange unit and uses external services to treat sulfate wastes

Solution 4 : The industrial uses both an ion exchange unit and evaporator

Data :

- hard chromium volume to be treated per year : $20m^3$
- $40m^3$ of diluted baths are used to compensate natural evaporation

The cost effectiveness of an ion exchange unit is strongly dependent to sulfate waste management

5. CONCLUSION

Many "clean" technologies exist to treat waste and pollution. Even if they can not reach alone the limits imposed by regulation, they can help to reduce pollution and waste normally treated by effluents treatment plant.

Each "clean" technology has its own field of utilization in limited working conditions. Users have to avoid to generalize the success or the failure of one application. Each case has to be considered as unique depending on users' specific parameters(surface finishing activity involved, productivity, volume and composition of pollutants, industry size, ···).

Sometimes case studies show unacceptable cost effectiveness. It could be deduced that it is better to keep producing waste than not. Nethertheless, this last remark can be proven false by using parameters more difficult to quantify such as : the increasing of process control, or the improvement of corporate image by being 〈environment friendly〉. The ISO 14001 certification will probably push some companies to use these "clean" technologies.

In every case it will be essential to verify if the chosen technology does not have any negative impact on both the productivity and the quality of surface finishing.

In conclusion it can be said, "test it before you go for it"