Chloride-Based & Chloride-Free Products For the Rotogravure Industry

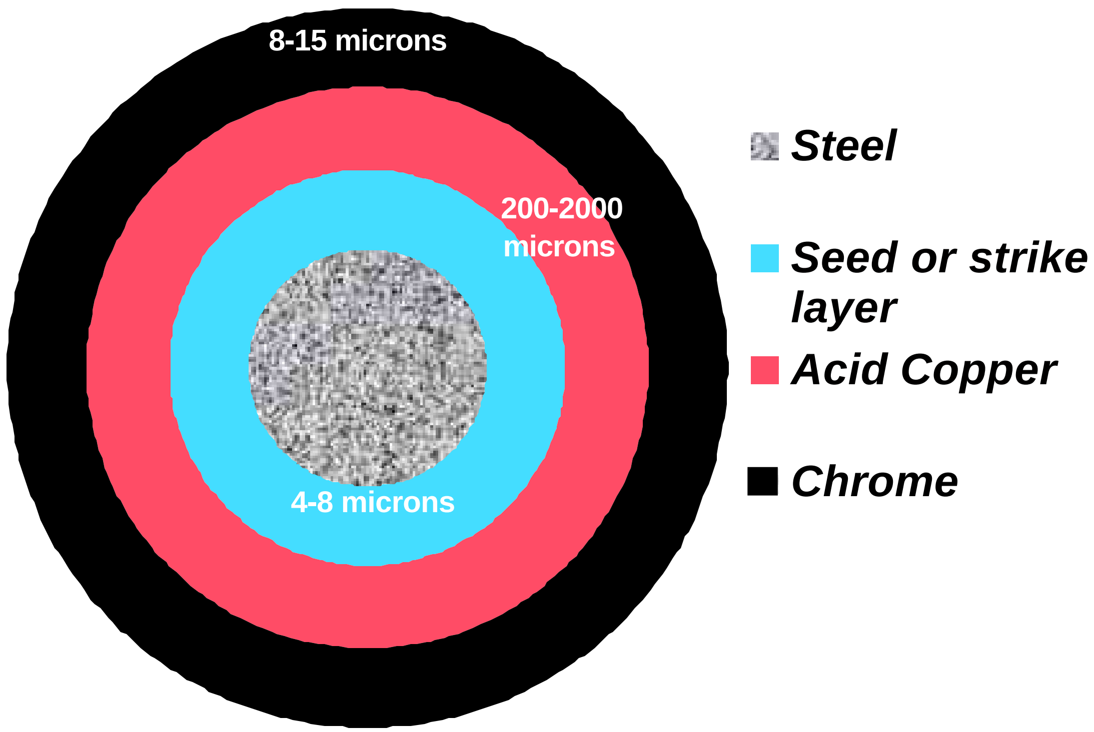
Grant Keers, MIMF, Atotech GmbH, Berlin, Germany

Rotogravure has its roots in the 15^{th} century. Artists could transfer their designs by hand engraving, enabling them to sell their wares commercially. The modern methods of engraving require the use of copper plating solutions to build a layer, which can be subsequently engraved, usually by electronically controlled diamond cutting. This paper will introduce rotogravure and explore the differences between conventional chloride-based chemistries and chloride-free acid copper plating processes. It will also look at the implications of new-generation, non-carcinogenic, chloride-free processes versus the historic thiourea-based chloride-free processes.

For more information, contact:
Grant Keers
Atotech Deutschland GmbH
Erasmusstrasse 20
10553 Berlin, Postfach 210780
10507 Berlin (Tiergarten)
011-49-1607-220653
Marida.Brandes@atotech.com

Rotogravure is a technology using copper and chrome plated rotating steel, aluminium or plastic cylinders to produce high quality visual images of consistent and repeatable quality at very high speeds.
Rotogravure has its roots in the 15th century with the need for artists to reproduce their designs commercially. The technology evolved through a variety of methods such as carbon grid screen transfer at the turn of the century, through photoresist etching technologies, up to the present day digitally controlled electronic diamond engraving. A cross section of a cylinder is shown below in fig.1.

fig.1.



Rotogravure serves a variety of industries such as:
Consumable wrapping; Confectionery, milk cartons, cigarette packets.
Decorative household design; Wallcoverings, textiles and floorcoverings
High quality publishing; Glossy magazines, Sunday supplements, comic books.

Cell Structure

The key to the whole rotogravure process is the quality of the "cell" structure. The cell is engraved into the copper plated surface prior to chrome plating. The walls of the cell must retain their stability in all dimensions. The edges of the walls must be clean and sharp to enable crisp, clear imaging to occur. Examples of cells can be seen below in fig's 1-3.

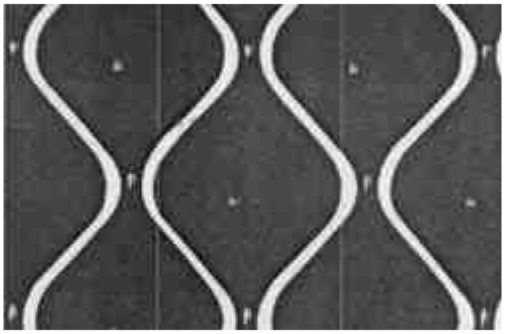


fig.2. Channel cell
Maximum ink fill

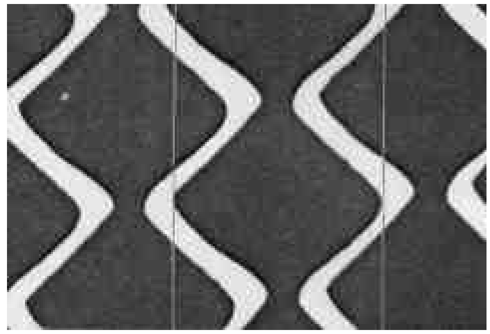


fig.3. Compressed cell
Medium ink fill

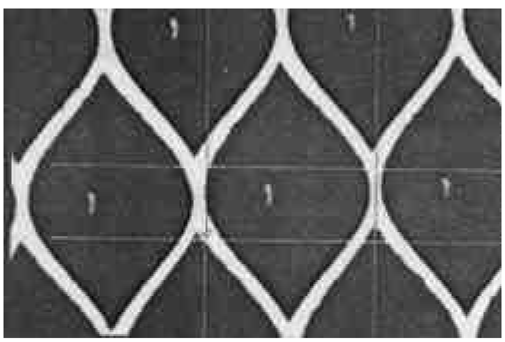


fig.4. Intermediate tone cell
Low ink fill

Technical positioning for a rotogravure cylinder

A rotogravure cylinder should have properties similar to the following criteria;

Copper plating

Hardness as deposited of between 200 and 230HV
Hardness loss after aging @140^{c} for 1 hour of no more than 5%
Elongation should be between 12 and 20%
Tensile strength around 70 KN/cm^{2}

Chrome plating

Hardness of between 950 and 1100HV
High level of micro-cracking to hold the ink –1000 - 2000 cracks/linear cm
Thickness of between 8 and 15 microns
Oxide in the deposit of around 0.75%
Low coefficient of friction – around 0.13

Alternative Production methods

We will discuss conventional polished and engraved cylinder production. However, there is an alternative technology called “ballard skin” processing. This was very popular with publishing companies in particular.
The process involves a steel base cylinder which is then copper plated to a certain thickness. This copper layer then has a very thin layer applied, for example an organic layer. The most widely used was albumen. Other methods such as applying a thin layer of metal such as immersion silver could also be used. These layers would let copper deposition occur but would inhibit any electrochemical/mechanical bond between the two copper layers. The cylinder would then go to be copper plated to its final thickness. After the desired thickness was achieved, the cylinder would be engraved, hard chrome plated and would then go to the printing press.
After the required length of print was produced, the copper skin would be slit and removed as a sheet. The cylinder would then be cleaned, further albumen applied and the process would occur over again.
This method enabled rapid turnaround of cylinders. But because the process produces a copper hardness of only around 150HV, it could not be used with the new generation fast electronic diamond engraving machines which require a copper hardness of at least 185HV usually 210HV. The image was always produced using chemical etching. Consequently, lower quality was accepted.

Substrates

All the current substrate technologies are based around steel, aluminium or new substrates such as plastic.
Steel has always been the traditional choice due to its wide availability and expansion characteristics with subsequent plated layers of copper and nickel. Aluminium is not widely used but has a small market share, usually in the USA due to its potential as a lightweight alternative to steel.
Plastic is a new potential substrate. The advantages of this are its light weight. This leads to much less wear and tear on the printing press. The difficulties involved with using plastic initially were due to the instability and mechanical resonance which would occur when the cylinder was being machined and engraved. As the diamond tool came into contact with the plastic, very subtle changes and flexing would occur in the plastic surface. This would continue to increase setting up a pattern of vibration which would eventually shatter the tool and seriously damage the cylinder face. Much work has been done in this area and there are now a range of plastic formulations which will meet the demanding machining criteria.

Pretreatment

The first stage of cylinder preparation is pretreatment. The usual process for all substrates is to clean and degrease the cylinder surface. After this, in the case of steel the surface is micro-activated using a mildly acidic solution. Thorough rinsing is required at all stages after which the substrate is conductively "seeded".
With steel a cyanide copper strike is used. A nickel strike can also be used. This is usually a watts or woods formulation although some companies use nickel sulphamate.

New generation alkali-non-cyanide copper strike solutions are now becoming available due to the global trend away from cyanide containing processes.
Aluminium is zincated using standard widely available chemistries, and standard plating on plastics pretreatment processing is employed for plastic metallization.

Acid Copper plating

After first stage metallization, all the cylinders go for acid copper plating. The acid copper step has certain key parameters. Chloride levels being the most important. Acid copper plating is done in a variety of processing methods, partially immersed semi-automatic, fully immersed semi-automatic and both partially and fully immersed automatic production. These different types of production require different chemistries. Usually, in semi-automatic partial immersion processing, the copper additive system is chloride containing.

The standard solution parameters for a partially immersed semi-automatic bath would be;

Copper sulphate-	210 g/lt	Range 190-230 g/lt
Sulphuric acid-	70 g/lt	Range 55-80 g/lt
Chloride ion-	70ppm	Range 50-90 ppm

The standard solution parameters for a "chloride free" fully automatic bath would be;

Copper sulphate-	210 g/lt	Range 190-230 g/lt
Sulphuric acid-	70 g/lt	Range 55-80 g/lt
Chloride ion-	***5ppm***	***Range 2-7ppm***

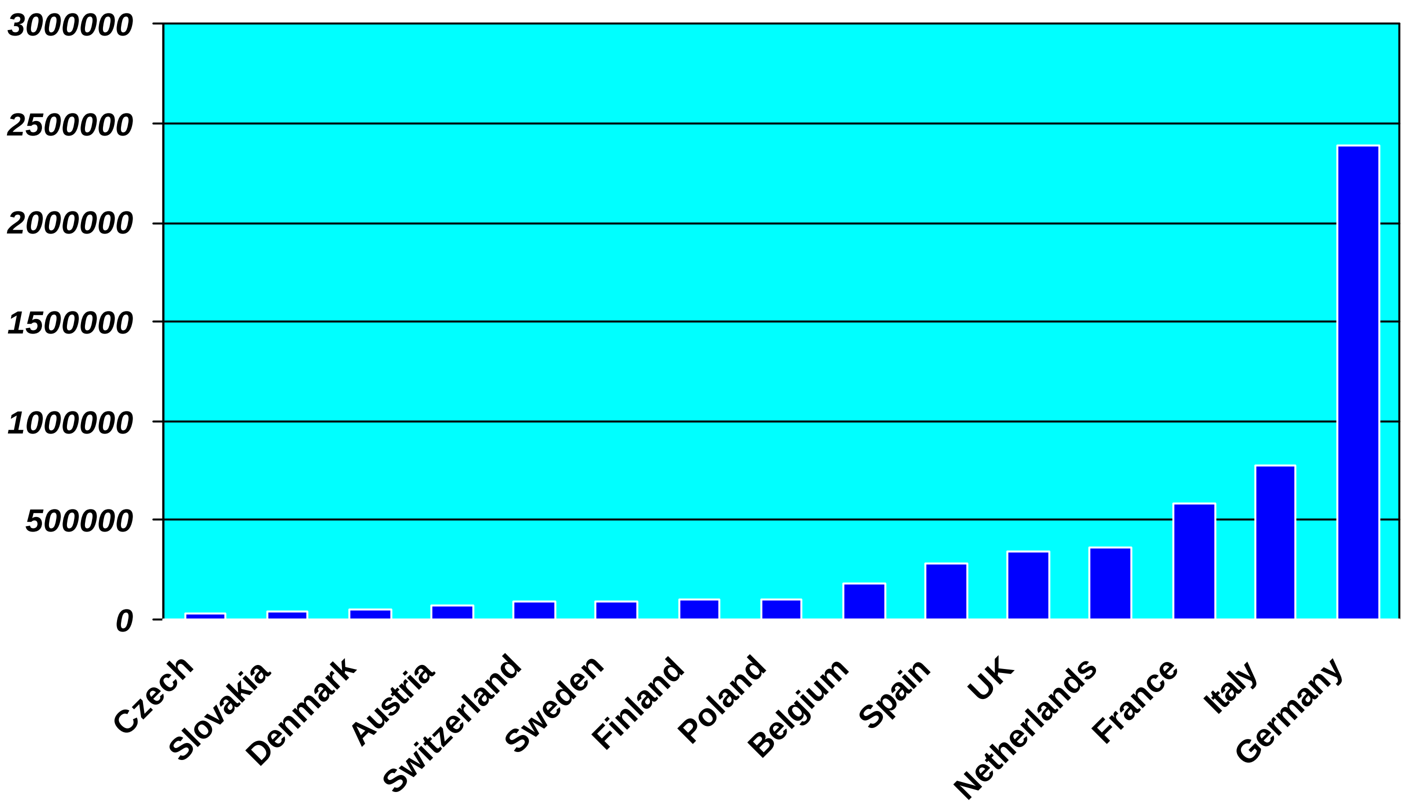
As can be seen, the statement "chloride free" is not an accurate one. There is always a need for a small amount of chloride in virtually all solutions. The requirement for this in the "chloride free" processes is to enhance levelling. However, the small amount necessary needed for this purpose, makes it very difficult to control.

Markets

Historically, the industry has always been split between chloride based and chloride free processes. This was due to the different market types globally.

The USA and UK always tended towards semi-automatic operation. The bulk of the rotogravure processing in these markets is consumable packaging. This would mean a wide and diverse range of cylinder dimensions in both length and width. Consequently, a high degree of flexibility in production was needed. Most of these types of plants are able to be adjusted for length and width of different cylinders.
Automatic plants were initially developed for use in the publishing sector where all the cylinder dimensions would be the same. The early market for automatic plants was continental Europe, primarily Germany. Germany has one of the worlds largest publishing markets, it is bigger than all the other European markets put together (see fig.5) As the publishing market uses the same cylinder types repeatedly, the consistent solution conditions of the automatic plant lend themselves easily to this market area.

fig.5.
European publishing capacity – paper tonnage



COURTESY OF THE EUROPEAN ROTOGRAVURE ASSOCIATION

<u>Technical standoff – Dye free, chloride containing, versus dye free, chloride free, versus dye containing, chloride containing additive processes... ZZZZZZZ!!</u>

Chloride free – chloride based

Historically, the industry has always been split between chloride based and chloride free processes due to the different processing types. The main differences are the voltage and current density requirements. Semi-automatic partial immersion production requires around 8 volts with a current density of 15-20 a/dm^2. This will give a deposition rate of between 125 and 250 microns per hour. Fully automatic baths have a higher current density – between 20 and 30 a/dm^2 and a higher voltage, usually 10 volts or above. The deposition rates achieved in automatic production are between 200 and 400 microns per hour.
Anode cages for both processing methods are made of titanium. The voltage requirement used in automatic tanks in a chloride environment above 7ppm will destroy the anode cage. The rule of thumb is 9.4 volts with a minimum anode cathode ratio of 2:1 per solution will exhibit the problem.
This also happens in semi-automatic tanks if the power distribution is incorrect from anode cage to anode cage.

A single station automatic plant will cost around $300K , whereas a twin station semi-automatic tank will cost around $50K. Your production manager pays his money and takes his choice!!

The automatic plant manufacturer needs to have chemistry additives to improve levelling and stop the cylinders self annealing. In the 1960's it was determined that thiourea would accomplish this in conjunction with a surfactant. Thiourea is also very good in the HCD range to ease burning.
The main weakness apart from the poisonous nature of thiourea is the limitations of the chemistry in controlling the copper grain structure and consequent cell structure. Thiourea has a major influence on ductility of copper, if you use too much the copper structure becomes brittle and difficult to machine. Common problems are "venetian blind" effect. If you use too little, the cylinders will self anneal very quickly. The working window with thiourea based systems is very limited.
Chloride based additive processes are from similar chemistry families to thiourea but are not as hazardous.
The benefit of chloride based processes is their ability to give a wide range of processing parameters. Generally, by adjusting the additive levels in the solution, you can engineer the copper structure to whatever qualities you are looking for. These additive systems are also developed to work in the HCD to ease burning. However, unlike the thiourea additive systems, you can have a wide working window without impacting too heavily the copper structure. These systems if used in a correct manner will also keep their hardness for a long time. ***One of the leading available systems will not self-anneal inside 36 months.***

Dye free – dye based chloride containing additives

The dye based chloride containing additive systems were developed as an offshoot of standard decorative copper plating additives. They simply use the co-deposited organic to give a high gloss to the surface prior to machining.
These systems have serious problems in controlling copper grain structure, as you are relying totally on the organic contamination in the deposit and brightness is the primary criteria. However, the main problem with the dye containing system is that the cylinders will self anneal very quickly, in some cases they will fall from 210HV to around 150HV or below in 5-7 days. At 150HV the cylinder cannot be electronically engraved and will need to be reprocessed.
It has always been the case that the customer likes to see a bright copper surface from the tank, but with rotogravure cylinders, this is not necessary as the cylinder is subsequently polished to a very high gloss by machine. Polishing is carried out to make sure a consistent thickness across the face length is established. The usual aim is less than 25 microns RA from end to end of the cylinder.

New generation, non-thiourea based chloride free additives

As thiourea becomes more and more proscribed, particularly in Europe alternative technologies are becoming more and more necessary.
The main difficulty with producing alternatives is the historical use of thiourea, its economical cost and wide availability. There is a tremendous market potential for a sufficiently high quality chloride free process that does not contain thiourea. Of course, any process should aim for an improved working window compared to thiourea and should approach dye-free, chloride based chemistries in performance.

I will give an overview of some work now being carried out in this field.

One particular process has been under trial for some time. It has so far met many of the requirements needed for a process with suitable quality. It gives a very nice copper structure at the engraving stage. So far cylinders produced in the process do not show problems with self annealing. The process has been under test for around one year and so far no cylinders have relaxed.
A tremendous amount of work has been carried in characterising this process. As mentioned earlier one of the main issues is self annealing of the copper deposit.
It has long been known that subjecting the copper surface to heat will tend to accelerate any latent tendency to relax.
The following tables (fig.6+7), show the relationship of varying additive concentrations against the hardness value obtained. The chart contains out of tank hardness and hardness after heat aging at 140^{C} for 1 hour. As can be seen the copper surface remains remarkably constant during this test.
As can be seen, an interesting observation is that the hardness is not unduly influenced by over dosing additives. The normal level in the solution would be around 2-4 mls/lt. But even

at 15-25 mls/lt, the hardness remains constant at around 250HV. After heating, to potentially reproduce the self annealing tendancy, the hardness value only falls by around 5% showing the excellent stability of the copper deposit.

fig.6.

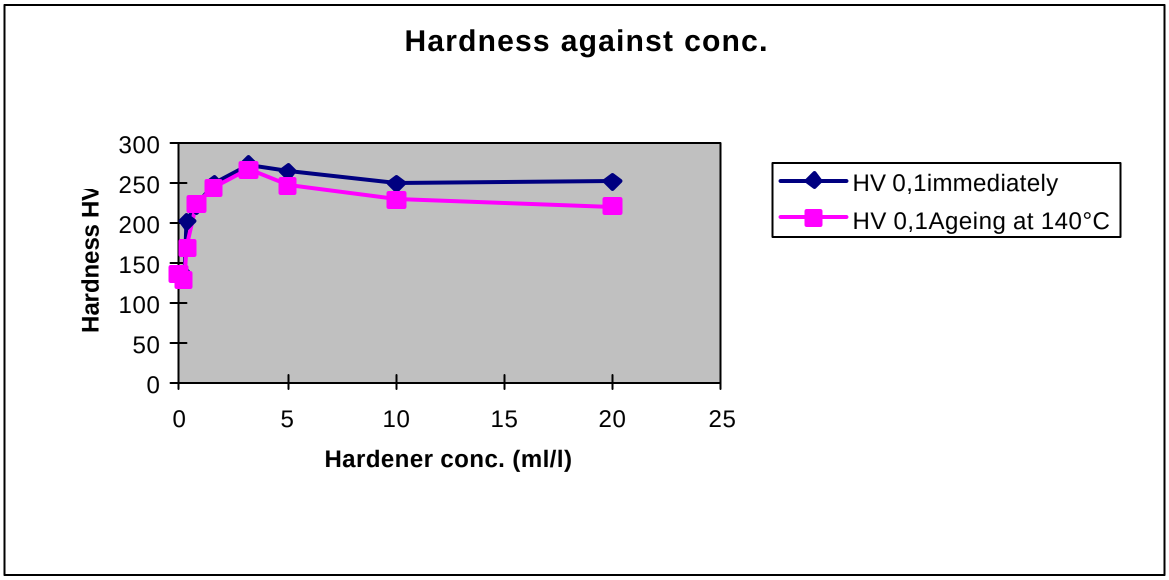
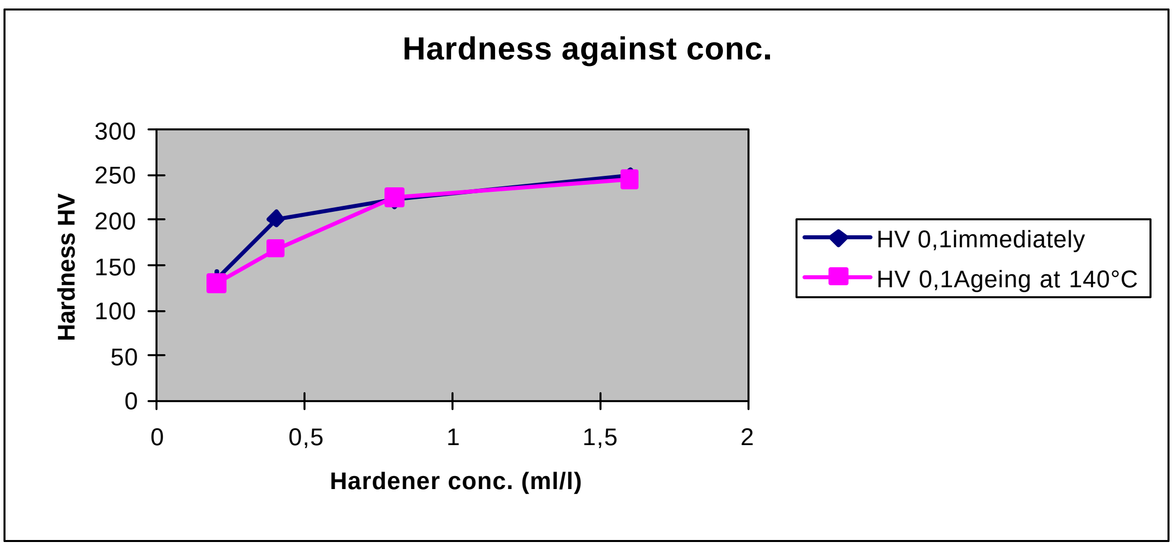


fig.7.



Conclusions

It is clear as Europe leads the way that products such as thiourea will become proscribed in the rest of the world. There will be a continuing need to maintain and increase the quality of the engraving of the rotogravure cylinder and investigate alternative substrates and methods of production.
The company that can improve chemical technology and at the same time continue to adopt an environmentally responsible approach to their products, will have a significant market impact now and in the future.

References

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