UTILIZZAZIONE DEI SOLVENTI CLORURATI COME AGENTI DI LAVAGGIO NELL'INDUSTRIA METALMECCANICA ED IN PARTICOLARE NELLA PRODUZIONE DELLE PUNTE IN OTTONE PER ARTICOLI SCRIVENTI

THE USE OF CHLORINATED SOLVENTS AS WASHING AGENTS IN THE METAL AND STEEL INDUSTRIES, AND PARTICULARLY IN THE PRODUCTION OF BRASS POINTS FOR WRITING INSTRUMENTS

REINOL®

UTILIZZAZIONE DEI SOLVENTI CLORURATI COME AGENTI DI LAVAGGIO NELL'INDUSTRIA METALMECCANICA ED IN PARTICOLARE NELLA PRODUZIONE DELLE PUNTE IN OTTONE PER ARTICOLI SCRIVENTI

THE USE OF CHLORINATED SOLVENTS AS WASHING AGENTS IN THE METAL AND STEEL INDUSTRIES, AND PARTICULARLY IN THE PRODUCTION OF BRASS POINTS FOR WRITING INSTRUMENTS, WITH ASSOCIATED PROBLEMS

Massimo Gippa
Pietro Buzzetti

THE USE OF CHLORINATED SOLVENTS AS WASHING AGENTS IN THE METAL AND STEEL INDUSTRIES, AND PARTICULARLY IN THE PRODUCTION OF BRASS POINTS FOR WRITING INSTRUMENTS, WITH ASSOCIATED PROBLEMS

First Section
Introduction

This document is intended to analyse the various problems related to the use of solvents known as chlorine derivatives and to sensitise users to their correct use with the aim of preventing corrosion in the final products.
This section will focus on the characteristics of chlorinated solvents normally used to degrease metals and on the problems that might accidentally follow the inappropriate use of the product.
The second section will concentrate on possible problems arising from the use of uncontrolled solvents.
A thorough analysis of the issue was made necessary by various defective cases registered all over the world in the last two years. Refills manufactured and sold were then rejected by final customers because they just stopped writing. Cases of that kind had never occurred before, nor was the origin of the defect known.

Chlorinated solvents and problems related to their use

Chlorinated solvents were introduced in the cleaning and degreasing of metals at the beginning of the Sixties: they are the most important class of substances belonging to the family of halogen derivatives. They replaced conventional oil products (special petrol and white spirit) with the disadvantage of being inflammable whilst chlorinated solvents are not.
They are polar substances endowed with a remarkable solvent power.
Chlorinated hydrocarbons usually possess a high solvent power with greases, rubber, chlorine, etc.
They are insoluble in water but can be mixed with other solvents; their sweetish smell is stronger than that of unchlorinated solvents.
It can be stated that chlorohydrocarbons are currently the main means through which chlorine is fixed and reaches the chemical market.
Chlorinated hydrocarbons can e subdivided into three main groups:
- Paraffin derivatives
- Derivatives of unsaturated hydrocarbons
- Derivatives of aromatic hydrocarbons

Chlorinated solvents are technically divided into:
Chloroethanes
Chloroethylenes
Chloromethanes
We will confine our analysis to compounds used in the metal and steel industry as degreasing agents for metals.

Chloroethanes
There are nine chlorinated solvents deriving from ethane; their constitution varies according to the number of chlorine atoms present in replacement compounds.

1,1,1-Trichloroethane
Thanks to its low toxicity this solvent has taken up a remarkable importance in the cleaning of metal parts.
It is hydrolysed by hot water under pressure; the type of acid generated depends on the amount of water reacting with the solvent; more specifically the hydrochloric acid which is produced caused a significant corrosion.

Chloroethylenes

More commonly known as Chlorothenes, these are six chlorinated products derived from ethylene by replacement of one or more hydrogen atoms with chlorine atoms. The most widely used types are:

Perchloroethylene
It is conventionally used for the degreasing of metals.
It is not stabilised and exposed to water and light it can undergo a slow oxidation process with consequent release of toxic and corrosive substances.

Trichloroethylene
It is commonly used in metal degreasing.
In the absence of inhibitors or stabilisers, Trichloroethylene slowly oxidises in contact with air and generates hydrochloric acid, thus becoming corrosive with all metal surfaces.
Impurities contained in this chlorinated solvent are not allowed to exceed 10 parts per million acidity, 10 parts per million insoluble residue, and what is very important, 100 parts per million water.

Chloromethanes
They are four products obtained from the gradual replacement of methane hydrogen atoms with chlorine atoms. The most well-known is Methylene Chloride.

Methylene Chloride
Methane chlorinating has a specific importance and interest because it is the only technology allowing for the production of all the series terms.
Because of its high volatility, it is not normally used in metal degreasing.

Table 1

	Flash Point	Molecular Weight	Boiling Range (°C)	density (20°)
Methylene Chloride	Not Inflammable	84,94	Between 39,5 and 40,3	1,330
Perchloroethylene	Not Inflammable	165,85	Between 120 and 122	1,623
Trichloroethylene	Not Inflammable	131,40	Between 86 and 87,5	1,464
1,1,1-Trichloroethane	Not Inflammable	133,42	Between 73 and 75	1,320

Cleaning Processes
The following factors should be taken into consideration when choosing the most appropriate cleaning method:
- Cold processes, though being direct and not requiring special equipment or technologies, lead to a high loss of solvent during the mechanical action accompanying the process and carry the risk of polluting the surface,
- Processes based on heat, besides allowing for solvent re condensation and therefore reuse, have a greater cleaning efficacy.
During solvent re condensation however, there is the danger of a greater concentration of water.
The most widespread degreasing methods in industry are as follows:
Hot degreasing with solvent vapours
Cold degreasing by shaking, immersion, sprinkling
Ultrasound degreasing

Ultrasound degreasing
This is the method affecting the sector of writing instruments directly and therefore the method we will be dealing with in this document.
It is well-known that the motion of the cleaning solution or of the object to be cleaned improves and accelerates the cleaning process. Ultrasounds are a practical application of this theory.

Ultrasound energy is by definition a high frequency mechanical vibration: a 50 hertz alternating current is sent to a generator developing a frequency of 20.000 cycles a second, or even higher. Transducers turn electric power into sonic energy and then into sound waves; the latter are further transmitted to a fluid, thereby generating cavitations.
The cavitation mechanical action coupled with the solvent chemical action produce an effective degreasing process.
Ultrasounds start to remove fuel oil deposits and solids adhering to metal surfaces that are usually insoluble in conventional solvents.
Ultrasound cleaning is particularly useful for the removal of impurities in areas difficult to access.
In order to ensure an optimal ultrasound degreasing, operating temperatures should be 10-20°C lower than the solvent boiling temperature.

Main features of solvents used for metal degreasing
The main features of these solvents are:
a) Non inflammability: it is one of the main reasons why they are industrially used to degrease metals.
b) High solvent power: they can solve all kinds of greases, oils, waxes and resins used in the metal and steel industry during the production process.
Along with positive features we should like to mention some negative ones, and namely:
a) They are reactive to metals: chlorinated solvents, if not appropriately stabilised, may cause corrosion, stains and oxidation in metal parts.
b) They are unstable in the absence of inhibitors.

Precautions in the use of chlorinated solvents
Water contamination
Water contamination is the most common cause of corrosion.
When a mixture of any chlorinated solvent and water comes into contact with metal parts, corrosion may occur.
Corrosion occurring inside the degreaser may also stem from thermal decomposition and the consequent formation of acid. This situation may be caused by a solvent overheating locally because of an excessively high temperature of the irradiating surfaces; it may also stem from high boiling point caused by too much oil.
The formation of acid (induced by hydrolysis of the solvent used) may also be the result of inadequate cleaning and maintenance of the equipment.
The careful removal of water that happens to be in the solvent is of the utmost importance to avoid the following inconveniences:
- Condensation of air moisture in the heating coils used for solvent re condensation.
- Presence of aqueous emulsions of blending oils on the parts to be treated.
- Presence of water on machined parts.
To avoid all this, each machine used for washing should be equipped with a very effective water separator.
Moreover, the amount of water present in solvents should be kept under 200 PPM; when this amount increases and reaches 450 PPM (which corresponds to 450 grams of water every 1000 litres of solvent !) the solvent must no longer be used but immediately distilled or passed through a water separator.
To confirm this, suffices to mention that the aqueous extract of a solution of 10 cc of stabilised but old 1,1,1-Trichloroethane with 90 cc of water at ambient temperature moves from pH 7 to pH 4 in 24 hours; with the increase in temperature, the pH goes down to 3.
If the same solution is exposed to sunlight for 48 hours, it reaches a very high acidity (pH 2,8).
It should be considered that water together with solvent may form an azeotropic mixture, that is a mixture of two or more liquids with a constant boiling point, that does not change composition, not even after a distillation.
A binary mixture may be characterised by a boiling point lower than that of the most volatile component and higher than the least volatile one.
It is because of the danger on introducing water into the tank that the machine must have a water separator with a capacity proportional to its working capacity.

Furthermore, to make separation easier, operating temperature should be decreased so as to reduce solvent solubility in water.
Table n.2 shows a number of parameters related to water-solvent azeotropic mixtures.

Table 2

	Azeotropic water-solvent mixture boiling point (°C)	Azeotropic mixture weight percentages	Corresponding to (ppm)
Methylene Chloride	38,1	1,5 water 98,5 solvent	15.000
Trichloroethylene	73,3	5,4 water 94,6 solvent	54.000
Perchloroethylene	87,8	15,8 water 84,2 solvent	158.000

Thermal decomposition
No chlorinated solvent should be used when there is even the slightest likelihood that vapours in a given pp concentration might come into contact with live flame, when surfaces are too hot, or when a distillation with too much oil or too little solvent has been carried out. This may lead to decomposition with the subsequent formation of hydrochloric acid, chlorine, carbon dioxide, carbon oxide and phosgene.
Luckily, the irritating action of hydrochloric acid clearly indicates the beginning of this decomposition, long before phosgene concentration reaches dangerous levels.
It should also be kept in mind that besides causing toxicological problems, decomposition by-products corrode the metal parts they come into contact with. Table n.3 shows that the starting temperature of thermal decomposition is higher for Trichloroethane than for the other chlorinated solvents conventionally used in metal degreasing. Moreover, Trichloroethane produces by far fewer decomposition toxic substances.

Table 3

	Thermic decomposition starting temperature (°C)
1,1,1-Trichloroethane	163
Trichloroethylene	120
Perchloroethylene	140

Evaporation
The choice of too volatile solvents like Methylene chloride should be avoided for two main reasons:
1) In certain atmospheric situations, steam contained in the air may condense on the metal surfaces cooled by the quick solvent evaporation and consequently increase water concentration;
2) An excessive solvent evaporation leads to a sudden increase in the water-solvent ratio.
In both cases an azeotropic mixture may be the result.

Storage
Solvent drums must not be kept for long in humid places to avoid a possible corrosion of containers and the subsequent solvent contamination.
As far as the storage in tanks is concerned, excellent results are obtained with stainless steel tanks with lined internal walls, so as to avoid any possible corrosion due to moisture.
Before using a container to store chlorinated solvents, one must make sure it is clean, dry and free from rust or metal chips, or from any oil traces that might trigger deterioration processes.

Distillation
Here are important instructions to be followed in the distillation of chlorinated solvents:
a) Separate the water layer that might possibly cover the solvent before carrying out distillation.
b) Remove possible chips and powders from the solvent before distillation.
c) Collect the contaminated solvent into clean stainless steel or plastic containers, since the presence of rust may catalyse the impoverishment of stabilising agents.

d) Use a system of stabilisers with a boiling point as close as possible to the solvent boiling point so that both go together during distillation.
Inhibitors present in chlorinated solvents play an essential role in reducing the risk of metal oxidation.
An incomplete distillation or insufficient equipment cleaning frequency may lead to an excessive loss of inhibitors during solvents utilisation or distillation.
A regular re-stabilisation of chlorinated solvents is very important to avoid corrosion and oxidation.
For this reason every user must carry out a check at regular intervals to assess the amount of stabiliser necessary to protect chlorinated solvents from acidification.

Regenerated solvents
The purchase of regenerated chlorinated solvents in the market may help you save money but may also cause inconveniences to the user if he is not informed well enough. Indeed it should be remembered that even a chlorinated solvent only partially degraded after distillation may become acid and therefore corrosive, with serious damage both to the equipment and, more frequently, to metal parts.
The best way to avert these risks is refraining from buying regenerated solvents from unknown sources or reckless suppliers.
Even a "home made" regenerating must be carried out with high-quality solvents; it is a simple operation, but it requires some attention and skills.
Remember that washing baths should never contain brass chips or powder (if present they must be promptly removed) since they catalyse the decomposition process.

Checks
Regular checks are recommended by all solvent manufacturers to maintain the cleaning system in optimal conditions and to ensure effective degreasing operations.
Some of these checks are very simple and do not require special equipment or chemical know-how; they can be carried out by the operators themselves.
Here are the most well-known control methods:
Acid acceptability test
Scratch test
Aqueous extract pH test
The scratch test is generally used to assess the stability of solvent with aluminium and therefore it does not fall into our scope of analysis; the acid acceptability test is normally used to assess the amount of stabiliser present necessary to protect the solvent from acidification.
The simplest method known is the aqueous extract pH test; the necessary material can easily be found.
To carry out this test put 50 ml of chlorinated solvent in a clean container previously rinsed in distilled water, add the same volume of distilled water previously brought to pH 7 with a normal-hundred HCl solution, and shake for about two minutes.
Leave to separate and finally dip electrodes of the pH-meter into the water and measure.
The pH should be as close as possible to 7. Lower values indicate that the acidification process has already started and that the solvent must therefore be regenerated.
All manufacturers can rely on laboratories with qualified experts at the customers' disposal for technical tests or consultancies; users may even be supplied a "test kit" for a quick and easy assessment of solvent stability.

Toxicity
Every person responsible for the operation and maintenance of degreasing equipment based on the use of solvents should be well-trained to its correct use.
Every user should precisely know all the risks related to the use of chlorinated solvents; it is only this way that, with some precautions, they can be used safely.
Trichloroethylene and Perchloroethylene are marked by a similar photochemical reactivity, but Trichloroethylene develops a significant amount of photo-oxidation derivatives which may lead to the release of a photo-chemical "smog".
Among these products, the most important one are: chlorine, hydrochloric acid and phosgene.

The most dangerous one is phosgene; besides being highly toxic, it has no property based on which it can be identified and has delayed toxic effects.
Not in all chlorinated solvents the decomposition process releases an amount of phosgene hazardous for health.
Trichloroethane for instance releases very limited amounts of phosgene and only during arc-welding processes.
Users of chlorinated solvents are highly recommended to abide by the following vital instructions:
Use solvents with a limited toxicity.
Use of appropriate and controlled equipment.
Use of distillation plants.
Development of preferential business relations with solvent manufactures able to guarantee an excellent technical service.
Table n.4 shows the toxicological properties of chlorinated solvents most commonly used in metal degreasing.

Table 4

	Smell			Effects			
	Perceptibility threshold (ppm)	Weak (ppm)	Irritating (ppm)	None (ppm) (8 hours)	Eyes Irritation (ppm)	Respiratory Diseases (ppm)	Coordination Lack (ppm)
1,1,1-Trichloroethane	100	350	1.000	500	1.000	2.000	1.000 (30-70 min.) 1.500 (15-60 min.) 2.000 (5 min.)
Trichloroethylene	100	200	600	100	400 (weak) 1.000 (strong)	1.000	400 (20 min.) 1.000 (6 min.)
Perchloroethylene	50	150	400	100	400	600	200 (8 hours) 400 (2 hours) 600 (10 min.)

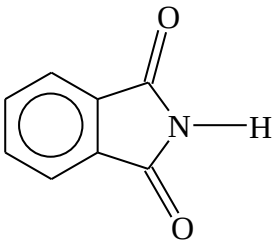
Production control and use of chlorinated solvents
In November 1992 in Copenhagen, during the fourth Meeting of the European Community, the application rules of the Montreal protocol were modified. The protocol laid down the rules to be followed in production control and use of Chlorofluorocarbons, Hydrochlorofluorocarbons, Carbon Tetrachloride and Trichloroethane.
Trichloroethane had already been included in the group of products regulated by the 2° Review Meeting held in London in June 1990.
Here are Trichloroethane control measures according to the latest application rules:
Production freeze: January 1, 1992 at 1989 levels
50% reduction: January 1, 1994 at 1989 levels
Total elimination: January 1, 1996.
The only derogation still in force apply to Underdeveloped Countries to meet the needs of their domestic markets.
It should be noted that the Montreal protocol provides for general rules only, therefore some countries might decide to set more restrictive rules to accelerate the reduction and elimination of Trichloroethane.

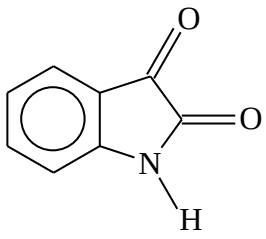
Second Section
Problems related to the use of chlorinated solvents in the production and utilisation of tips for ball-point pens.
The first part of this document has provided a broad illustration of metal degreasing methodologies and of the problems that might arise in the utilisation of chlorinated solvents.
This second part will analyse the practical implications of a number of problems recently emerged in the production of refills.

At the beginning of 1993, talking to a solvent technician working for a multinational company in the sector of chlorinated solvent production, we learnt that two years ago approximately all chlorinated solvent manufacturers had to give up the use of stabilisers like 1,4-dioxan because of toxicological problems. Such stabilisers were deemed highly toxic because of their very dangerous vapours. Moreover, dioxan is considered noxious to the mucous (eyes and lungs) and is absorbed by the skin.
All the problems occurred in the production of refills all over the world which caused a lot of troubles to both users and manufacturers date back to that period, but only very recently an explanation could be found.
All industrial sector using chlorinated solvents to degrease metals ran into the same problems.
The identification of their cause was neither simple nor immediate; solvent manufacturers did not have sufficient information at their disposal and the problem was totally unprecedented. Up to that moment REINOL had never encountered problems in the use of inks for ball pens.
Several tests were carried out both internally and by external laboratories to come to a correct data interpretation. They were made necessary by the far-reaching implications of the issue and by the difficulty in finding a solution.

Analysis of the first anomalies occurred and search for the cause of writing blocking.
The first complaints arrived in July 1991; a Korean customer complained for the presence of defective refills: they usually started to write, but after a while, the writing specimen became irregular until it totally stops.
By insisting on moving them some refills started to write and became gradually normal again.
The stop of writing into the refills is normally due to the following reasons:
1) The ink thickens and increases viscosity.
To check this instance, our laboratory measured viscosity with a computerised viscometer Haake Rotovisco Rv-20 equipped with a PK5-1.0 probe.
Thanks to this equipment our laboratory is able to carry out the analysis of ink viscosity even with a limited number of refills.
The ink of these defective refills revealed value in compliance with the warranted characteristics.
2) Ink crystallisation.
We analysed at the microscope a counter sample of ink sent back by the customer, but no crystallisation was observed; the ink on the slide was limpid and pure with no alteration.
3) Formation of a plug at the bottom of the tube due to a wrong ink formulation or to an early ageing on ink itself.
All tests carried out excluded the possibility that ink might have formed a dry plug at the bottom of the tube (in this case the consistency of ink was always normal) and also excluded the formation of corrosion in the tip shoulder area.
The latter observed at the microscope always appeared perfectly clean and free from any oxidation (see picture n. 1).

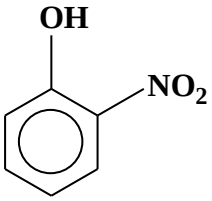
In this respect it is worth remembering that raw materials used in the production of inks are made of chemically pure compounds and their formulas are by their very nature constant and invariable; in the opposite case, their specific features would be totally upset.
In the case of dyes, for instance, the substance colour depends on the specific arrangement of atoms in the molecule.
All coloured organic substances are unsaturated compounds, that reduced with hydrogen loose their colour.
A few cases will now be illustrated to better explain the above-mentioned concepts:

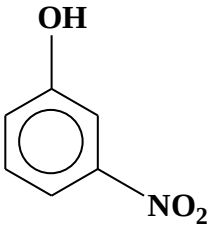


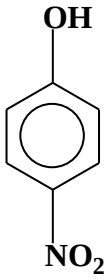


PHTALIC IMIDE ISATIN

In this case it was enough to change the arrangement of the -NH group and the carbonyl group (>C=O) to completely modify the characteristics of the product obtained (phtalic imide is colourless whilst isatin is orange).







YELLOW COLOURLESS COLOURLESS

To check the quality of the ink we replaced a number of tip with new ones and then proceeded to the various ageing tests.
All refills treated this way could write normally.
The only unexplored instance left was ink flowing in the tip internal duct and more specifically the ink close to the ball.
We carried out a new test in our laboratory, we removed the ball and collected the ink on a slide for subsequent observation at the microscope.
The ink turned out to be turbid, with unknown clotted particles.
Our customer carried out a well-structured laboratory test with the following results:
1) The ink analysed at the microscope was limpid.
2) The ink contained in refill tips had white insoluble spots(see Annex A: Customer's "TEST REPORT").
Moreover, tips showed a corroded area on their outer wall as it can easily be observed in pictures n. 2 and 3.
At the same time, when the first problems arose, our laboratory sent some refills to SGS Laboratories Ecology Department for a more accurate examination.

SGS Ecology
Technical evaluation
Possible metal enrichment of ink in contact with brass parts.
Since the defect (writing blocking) was believed to be due to the presence of brass powder not totally extracted during washing, zinc, copper and lead samples were taken from three different areas in the refill.
Three samples were obtained:

A- in direct contact with the ball
B- in the bottom part of the tip

C- in the polypropylene tube at 5-6 cm. from the tip.

The latter was considered the reference sample since it does not come into contact with the metal parts of the refill itself.
The different samples obtained were mineralised with an acid mixture (HCl -HNO3) and a hot process so as to destroy the organic matrix and produce a solution.
To check the presence of metals a plasma spectrophotometer with sequential reading was used.
Results showed (see Table n. 5 and Annex B) a greater concentration of the three metals in the bottom part of the tip which according to the SGS laboratory is due to the presence of brass powder caused by a "non perfect cleaning of the tip after the lathe operations". This powder creates a wider contact surface and increases the likelihood of brass mineralisation. To confirm or reject the assumption put forward by the SGS Laboratory we had to experimentally reproduce the defect in our laboratory.
To this aim, we formulated a number of different inks mixing with them some brass powder resulting from the tip lathe operations.
Refills assembled with these mixtures wrote with no defect at all, neither immediately nor after the ageing test.
Given the tiny amount of defective product, the analysis of A samples did not produce reliable results.
At this point, we had to go into greater details using an electronic microscope to find out the nature and origin of the clot inside the tip.
We entrusted the Chemical Laboratory of the Chamber of Commerce in Turin with this task.
With the aim of identifying the nature of the clots which are probably the root cause of the hole obstruction in our brass ball point refills, a scanning electron microscope (JEOL 6400) equipped with an EDS probe was used (X-ray energy dispersion spectrometer TRACOR Z-MAX 30). See Annex C.
The EDS analysis, as it can be easily observed (Chart n. 2 and Picture n. 18), highlighted as basic elements agglomerates of copper with zinc and chlorine. Their arrangement perfectly overlaps with that of the clot removed from the tip (see Picture n. 4).
In some cases the procedure highlighted only the presence of copper particles and this puzzled operators.
The same instrument was used to measure the various elements present in a brass tip free from corrosion (see Chart n. 1). In this case no particle of chlorine was observed.
After a first microscopic observation with a magnification power of x100, the magnification was increased to 1.500 to assess the crystalline structure of the elements making up the unknown agglomerate (see Picture n. 5).
Then we started looking for the element with the same crystalline structure observed at the microscope. After the analysis of several pure particles and artificially created products, the optimal result was obtained using some brass powder (see Picture n. 6).
The size of particles forming the agglomerates is about three micrometers and their crystalline structure matches that of pure electrolytic copper powder.
One of the doubts expressed by our experts referred to a possible contamination of ink at its finale stage, caused by an imperfect purification during the final stages of the production process. This could have led to an accumulation of insoluble particles inside the ball feeding duct during refill centrifugation.
To side-step this problem, one of the first checks carried out at the end of the production process is the centrifugation of some refills assembled with the ink under study. This operation which takes a long time (30 minutes approximately) is followed by a microscope analysis of the ink located behind the ball to verify the actual absence of insoluble parts.

To this purpose our experts prepared an X-ray 120 magnification map of insoluble residues obtained during ink purification at the centrifugation and filtration stage scattered in an area of 0,85 square centimetres (it should be pointed out that REINOL utilises a single process, with two filtrations and one centrifugation stage).
The map (see Annex C) highlights the presence of particles containing iron, silicon, calcium, sulphur and aluminium in a smaller percentage, and just one single copper particle.

If we compare the results of this map with the previous one, we can notice the actual efficacy of the purification process: indeed none of the particles present in residues is found in ink at its final stage.
Based on these results one could think that refills stopped writing because of an excess of brass powder or chips due to an insufficient cleaning and washing; however, the fineness of particles (3 micrometers) and the unusually high quantity could have been traced back to a bad washing of tips, but also to a cause which remained unknown for the moment.
The chlorine found during the EDS analysis (see Chart n. 2) was not taken into account at that stage simply because the hypothesis of corrosion had not been considered yet.

Verification of results and conclusions
Experimental test were needed to reproduce the same circumstances in the laboratory and to check whether the root cause of the writing defect was in brass contamination or in other substances normally used in the ball tip production process and in the subsequent refill assembly.
Inks were therefore contaminated with different percentages of the following products:
- very fine powder obtained from the machining of tips. Due to the greater surface in contact with ink, it is much more reactive than the tip brass;
- new blending oil used for the machining of tips;
- used blending oil with brass chips.
These mixtures were then used in the assembly of some control refills that were subsequently subjected to a number of tests, ageing tests included.
All refills thus obtained and assembled were operating perfectly. This meant that the writing blocking in defective refills was not due to the presence of brass (powder or chips) caused by a bad washing of the tip itself.
Some observations had already led us to think that the final explanation was to be found in a different direction, namely:
- The defect occurred both in tips supplied by experienced and excellent manufacturers and in products supplied by minor manufacturers with little experience in the field.
- The same defects recurred using ink supplied by different manufacturers.
During our study, we received refills from all over the world. They were filled with both our products and with inks supplied by competitors - they all had the same defect.
The time frame could be easily identified and it was the same for all manufacturers.
The EDS analysis clearly highlighted the presence of chlorine particles that do not belong to the composition of brass, nor to the formulation of inks.
The use of unwashed tips, dirty with oil, did not produce any defect, even after one year and a half of tests. Tips remain shiny and clean.
At page 49 Picture n. 7 shows a tip as it usually appears.
Our laboratory was developing a project for a very important customer. For the project it used ink formulated in the laboratory and tips of a very high quality. But there again, after about six months, all assembled refills stopped writing. This was the clue to look for different causes. The defect could no longer be ascribed to a bad ink formulation, that in this case had been produced in the laboratory with the help of precision micro-balances and therefore with an error rate of 0,001 grams for 100 g. of finished products !

The clue to the solution was provided by the observation of a number of tips with clear signs of acid corrosion on the inner duct of new tips coming from different manufacturers as it can be noticed in the following pictures:
- Pictures from n. 8 to n.15
- Picture n. 24
In this case corrosion is caused by the etching of hydrochloric acid formed through hydrolysis of the chlorinated solvent and is due to phenomena explained in the previous section.
It should be noted that hydrochloric acid is by far the most aggressive in etching brass followed by nitric acid, whilst sulphuric acid produces a weaker effect.
The term brass encompasses a wide range of Copper and Zinc alloys, where the latter is in a percentage not exceeding 50% (usually this percentage varies from 11% to 50%).
Zinc reacts easily to acid and develops hydrogen:

$$Zn + 2H^{+} <=> Zn^{++} + H_2$$

and

$$Zn + 2HCl <=> ZnCl_2 + H_2$$

The greater the amount of impurities in Zinc, the easier the above-mentioned reaction.
Zinc chloride is deliquescent substance, that is a highly hygroscopic salt with the property of turning into a solution by absorbing water from the surrounding atmosphere. This situation highly increases the reactivity of chloride itself.
Even copper melts in any acid if exposed to air.
With hydrogen halide acids, like for instance hydrochloric acid, copper oxide forms insoluble copper salts which precipitate:

$$2Cu + HCl <=> 2CuCl + H_2$$

This acid etching is followed by the formation of zinc, lead and copper salts.
Brass oxidation and the consequent formation of the so-called "saline efflorescence" leads to the formation of insoluble particles mixed with ink in the duct behind the ball. An example of this acid etching on brass, with the consequent formation of saline crystals, was already registered in nickel-plated tips at the end of the machining process in 1984 (see Picture n.17).
To avoid this problem, manufacturers started to machine tips only after the nickel-plating process.
In other cases acid etching may be caused by factors not linked to washing products but to the raw materials used during the forming process (Picture n. 17).
The ensuing copper and zinc oxides are highly reactive to certain ink ingredients and produce insoluble substances, usually copper and/or zinc carboxilates. These compounds alter the normal rheology of the ink, decreasing its ability to flow into the capillary duct.
The degeneration process occurs in three distinct stages:
Stage 1: At this stage a weakening of the writing specimen occurs; it is due to a narrowing of the tip inner duct and therefore to a smaller amount of ink flowing through.
Stage 2: Salts continue to increase with consequent writing "gaps".
Stage 3: It is the final stage of the degeneration process when tips just cease to write altogether.
Some refills however, if subjected to centrifugation, start to write again reasonably well, gradually improving until the ink flowing out has not brought out with it all saline particles.
The salt content of these refills is smaller and has not caused a total duct occlusion yet.
In refills which do not start writing again the salt content has totally blocked the capillary duct.
If we slightly blow the refills, writing starts and gradually becomes normal again. Even after ageing test, the performance of refills processed this way remains normal.
This is in line with the results of some tests carried out by our competitors. They demonstrated that by replacing or washing the tips of defective refills, but using the same ink, the problem did not crop up again.
Furthermore, there is the possibility that in some tip lots, the capillary duct might have already been totally obstructed.
In the light of these data, the results of all the tests carried out by external laboratories fine an easier explanation:
- The high copper and zinc percentage in the tip ink stressed by the SGS analysis confirms the high content of the two metals in ionic form, which therefore passes into ink.
- Copper and zinc particles found in all tests carried out by the Chemical Laboratory of the Chamber of Commerce are in fact Zinc and Copper salts, as it can be easily observed from Charts n. 1 (EDS analysis carried out on a brass tip with no writing defect: no chlorine, copper or zinc particle is found to be part of the brass alloy) and n. 2 (EDS analysis of the waxy clot behind the ball of a tip belonging to a defective refill: the two above-mentioned salts are not only made of copper and zinc, but also of a certain amount of chlorine.

- This explains why replacing the tips of defective refills with new tips all anomalies are avoided. Corroded tips probably account for a negligible and sporadic part of production.
To check the accuracy of our conclusions, we experimentally reproduced the defect in our laboratory. We dipped for few minutes some etch-free tips in a 0,1 normal solution of hydrochloric acid (which amounts to 3,5 g. of HCl dissolved in a litre of water). After a few days the tips had the same problems of those contained in defective refills; this is clearly shown in Picture n. 19 and 20.

Over a subsequent set of tests carried out at the Chemical Laboratory of the Chamber of Commerce, we tried to ascertain the origin of saline efflorescence using manifestly defective refills and tips coming from Korea.
Here are the findings of the analysis of saline formations:
1) Brass undergoes a selective oxidation of its components;
2) Displayed saline efflorescence is primarily made of Zinc and Lead salts.
Picture n. 21 and 22 are very helpful in explaining these findings.
At the same time a scanning electron microscope was used to observe a saline formation found in a recently produced tip (see Picture n. 23).
The EDS analysis clearly shows that this crystal is made of Zinc salts.

Chart n. 1
Result of the EDS analysis carried out on a new and corrosion-free brass tip.

Chart n. 2
Result of the EDS analysis carried out on the clot behind the ball of the tip of a defective refill.

Third Section
Photographic examination and subsequent discussion
After dealing with chlorinated solvents and their use as degreasing agents in industrial mechanical machining operations and more specifically going into the details of their application in the industrial sector of writing instruments, we felt it appropriate to carry out a case by case analysis of an issue involving manufacturers of all countries world-wide.
To avoid causing any damage to the manufacturers hit by this problem, we decided not to reveal the origin of defective tips and refills.
Her are the areas mostly affected by the defect:
- North America
- China
- Germany
- Centre America
- Italy
- Korea
- Sri-Lanka
- Thailand

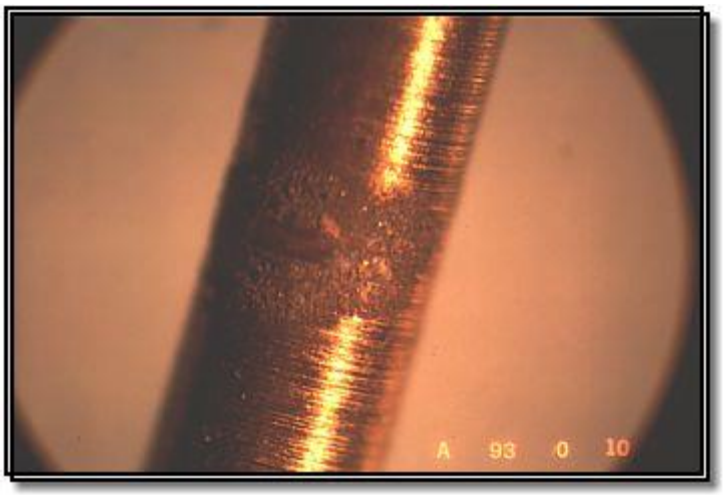
We would like to draw your attention on the fact these pictures account for only a part of all pictures examined and come from uniform lots in terms of the defect.

Fotografia nr.1
Repertorio Reinol A-93-0-3
Visualizzazione effettuata mediante stereomicroscopio.
Punta prelevata da un refill difettoso ripresa nella zona si spallamento.
E' possibile verificare che l'inchiostro presente non manifesta fenomeni di cristallizzazione ma é limpido e puro. Inoltre la corona della punta non presenta alcun attacco corrosivo dimostrando che l'inchiostro non ha reagito con l'ottone.

Picture n. 1
Reinol A-93-0-3 Series
The picture was taken from the screen of a stereomicroscope.
Tip removed from a defective refill in the shoulder area.
The tip ink is clear and pure without any sign of crystallisation. Moreover the tip crown shows no corrosion etching, meaning that ink did not etch the brass.

Fotografia nr.2
Repertorio Reinol C-92-12
Visualizzazione effettuata mediante stereomicroscopio.
Refills difettosi in cui é visibile un'ampia zona di corrosione anelliforme a livello della parete esterna delle punte.

Picture n. 2
Reinol A-92-12 Series
The picture was taken from the screen of a stereomicroscope.
Defective refills show a wide ring-like corrosion area in the tip outer wall.



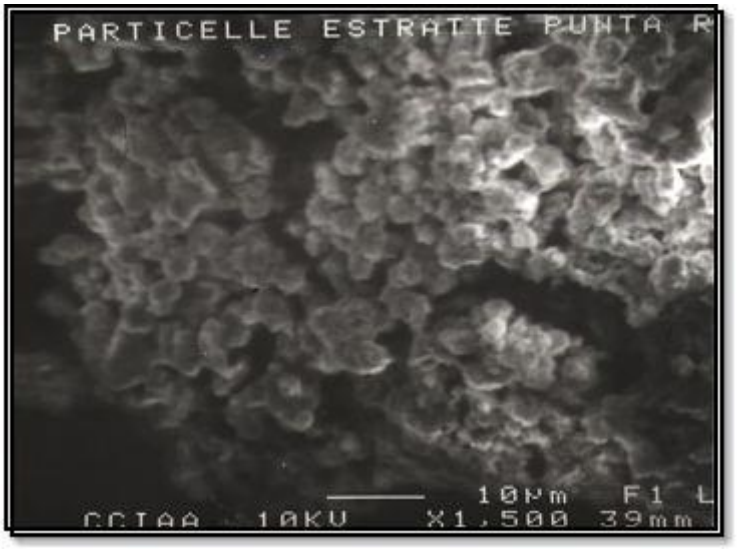
Fotografia nr.3
Repertorio Reinol A-93-0-10
Visualizzazione effettuata mediante stereomicroscopio.
Osservazione di una delle punte già riprese nella foto nr. 2 ad un ingrandimento superiore.
Notare l'efflorescenza salina (qui molto evidente) dovuta ad un'ossidazione selettiva dell'ottone con conseguente formazione dei sali dei 3 metalli principali entranti a far parte della lega stessa.

Picture n. 3
Reinol A-93-0-10 Series
The picture was taken from the screen of a stereomicroscope.

Observation of one of the tips already shown in Picture n. 2, with a greater magnification. Please note the saline efflorescence (very evident here) due to a brass selective oxidation with the consequent formation of salts of the three main metals making up the alloy.

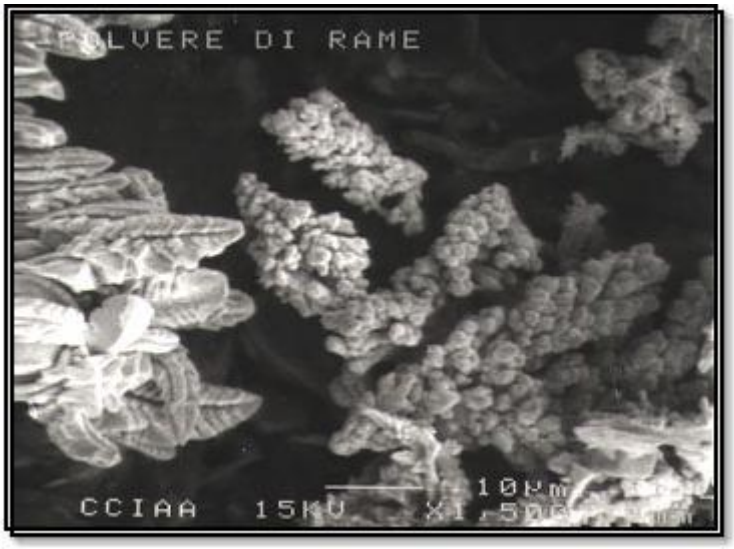
Fotografia nr.4
Repertorio Reinol-CCIAA
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 100 X.
Analisi del grumo di consistenza cerosa presente nell'inchiostro contenuto nella punta di un refill difettoso. E' possibile notare la differente struttura cristallina dei due rilievi in confronto con la parte circostante di materiale.

Picture n. 4
Reinol-CCIAA Series
The picture was taken from the screen of a scanning electron microscope using a magnification of 100x.
Examination of the waxy clot found in the ink of a defective refill tip.
Please note the different crystalline structure of the two profiles compared with the surroundings material.



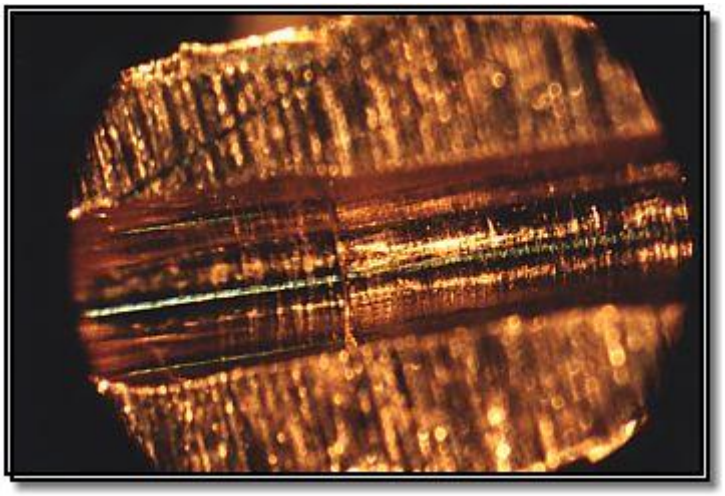
Fotografia nr.5
Repertorio Reinol-CCIAA
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500 X.
Analisi del grumo di consistenza cerosa presente nell'inchiostro contenuto nella punta di un refill difettoso di cui alla foto nr. 4.
Notare la struttura cristallina a elementi sferoidali delle particelle contenute nella massa in analisi.

Picture n. 5
Reinol-CCIAA Series
The picture was taken from the screen of a scanning electron microscope using a magnification of 1.500x.
Examination of the waxy clot found in the ink of the defective refill tip shown in Picture n. 4.
Please note the spherical crystalline structure of the examined mass particles.



Fotografia nr.6
Repertorio Reinol-CCIAA
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500 X. Polvere di rame.
Notare la struttura cristallina a elementi sferoidali del tutto simile a quella della foto nr. 5.

Picture n. 6
Reinol-CCIAA Series
The picture was taken from the screen of a scanning electron microscope using a magnification of 1.500x. Copper powder. Please note the spherical crystalline structure very similar to that shown in Picture n. 5.

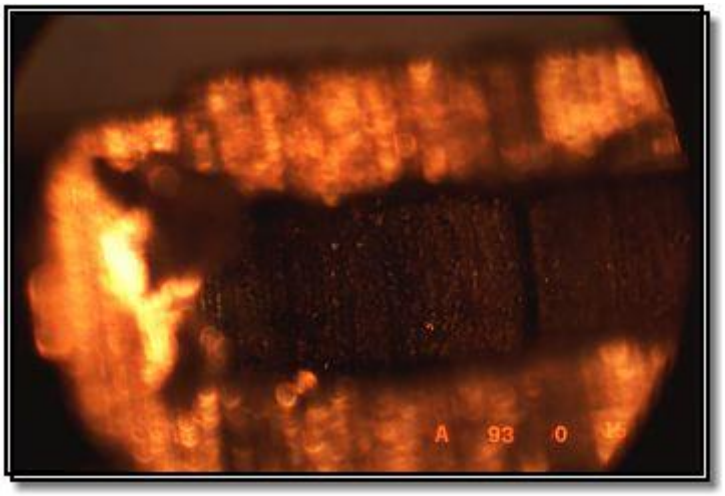


Fotografia nr.7
Repertorio Reinol 92-6560-00
Visualizzazione effettuata mediante stereomicroscopio.
Canale interno di una punta lavata che non presenta tracce di attacco corrosivo.
Notare la pulizia e la brillantezza del canale interno.

Picture n. 7
Reinol 92-6560-00 Series
The picture was taken from the screen of a stereomicroscope.
Internal duct of a washed tip with no trace of corrosion.
Please note the clearliness and gloss of the internal duct.

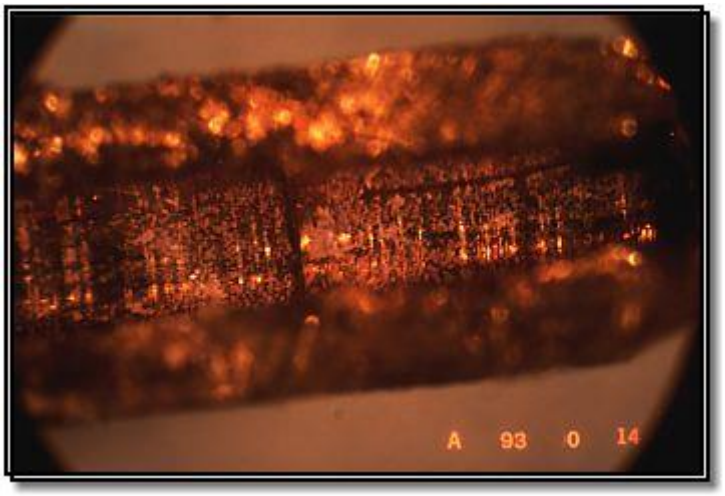
Fotografia nr.8
Repertorio Reinol 92-6560-0
Punta Tailandese
Visualizzazione effettuata mediante stereomicroscopio.
Canalino capillare in cui si può notare la forte opacità della parete che fa capire come l'attacco acido sia già iniziato.

Picture n. 8
Reinol 92-6560-0 Series
Thai tip.
The picture was taken from the screen of a stereomicroscope.
Capillary duct where you can see the marked opaqueness of the wall, indicating that the acid etching has already started.



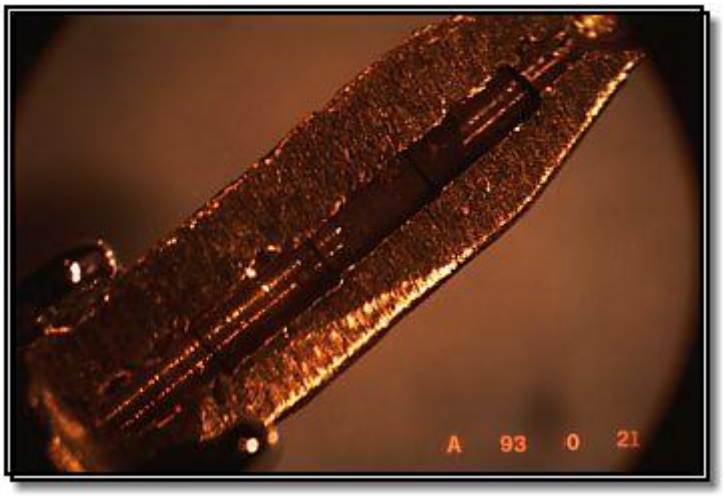
Fotografia nr.9
Repertorio Reinol A-93-0-15
Punta Tailandese.
Visualizzazione effettuata mediante stereomicroscopio.
Punta già osservata nella foto nr. 8 vista ad ingrandimento superiore.
Notare la formazione cristallina biancastra diffusa su tutta la parete interna.

Picture n. 9
Reinol A-93-0-15 Series
The picture was taken from the screen of a stereomicroscope.
Tip already observed in Picture n. 8 with a greater magnification.
Please note the whitish crystalline formation spreading all over the inner wall.



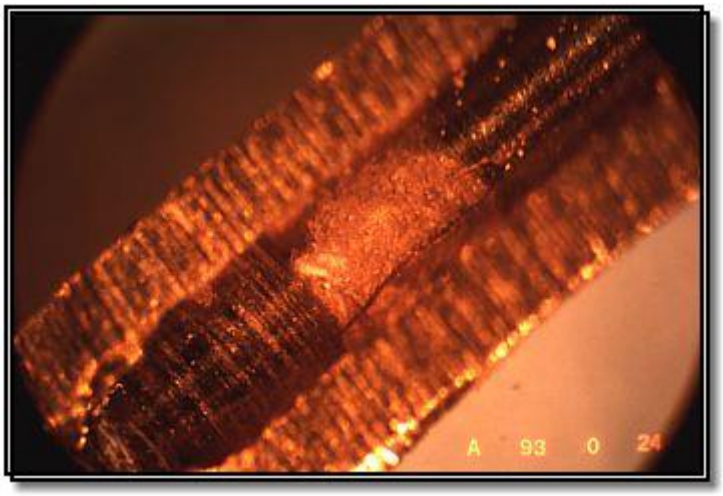
Fotografia nr.10
Repertorio Reinol A-93-0-14
Visualizzazione effettuata mediante stereomicroscopio.
Punta Coreana il cui canalino interno é invaso da cristalli biancastri corrispondenti a quelli già visti sul esterno di punte provenienti dallo stesso lotto di produzione di quelle con cui sono stati prodotti i refills visualizzati nella fotografia nr. 2.

Picture n. 10
Reinol A-93-0-14 Series
The picture was taken from the screen of a stereomicroscope.
Korean tip the inner duct of which is invaded by whitish crystals similar to those already observed on the outer wall of tips coming from the same production lot of refills shown in Picture n. 2.



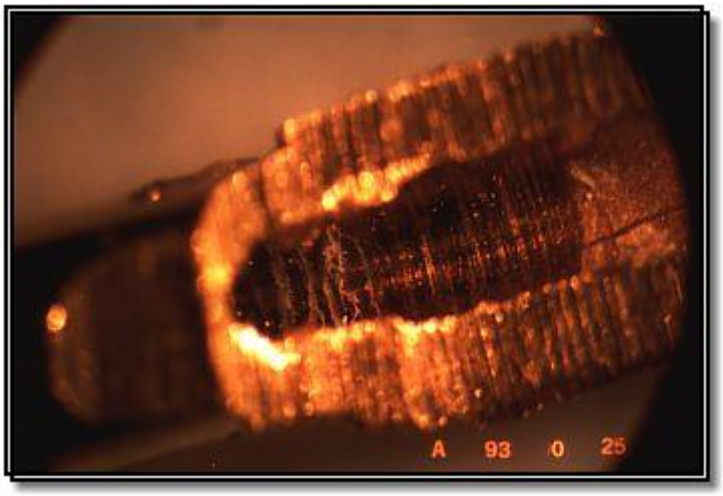
Fotografia nr.11
Repertorio Reinol A-93-0-21
Visualizzazione effettuata mediante stereomicroscopio.
Punta Italiana in cui si può osservare un forte attacco localizzato dovuto, probabilmente, al ristagno di una goccia di liquido al suo interno.

Picture n. 11
Reinol A-93-0-21 Series
The picture was taken from the screen of a stereomicroscope.
Italian tip with a marked local etching probably due to the stagnation of a liquid drop inside.



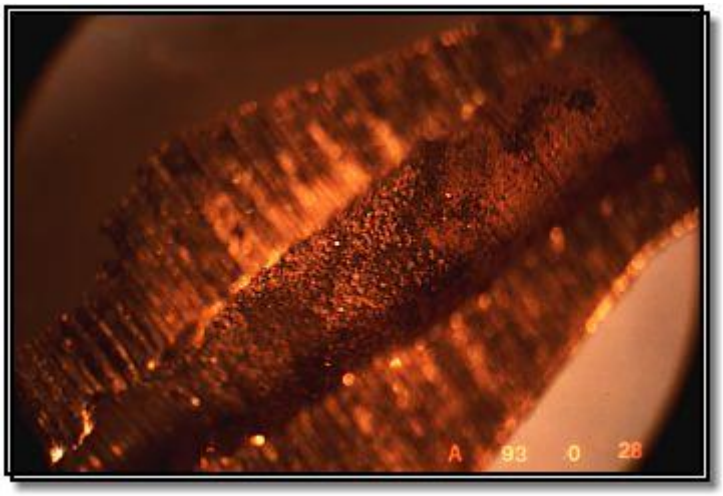
Fotografia nr.12
Repertorio Reinol A-93-0-24
Visualizzazione effettuata mediante stereomicroscopio.
Punta Svizzera in cui si può notare un forte attacco corrosivo localizzato dovuto probabilmente al ristagno di una goccia di liquido al suo interno.
In questo caso é possibile notare una notevole formazione cristallina.

Picture n. 12
Reinol A-93-0-24 Series
The picture was taken from the screen of a stereomicroscope.
Swiss tip with a marked local corrosion etching probably due to the stagnation of a liquid drop inside.
In this case a significant crystalline structure is to be observed.



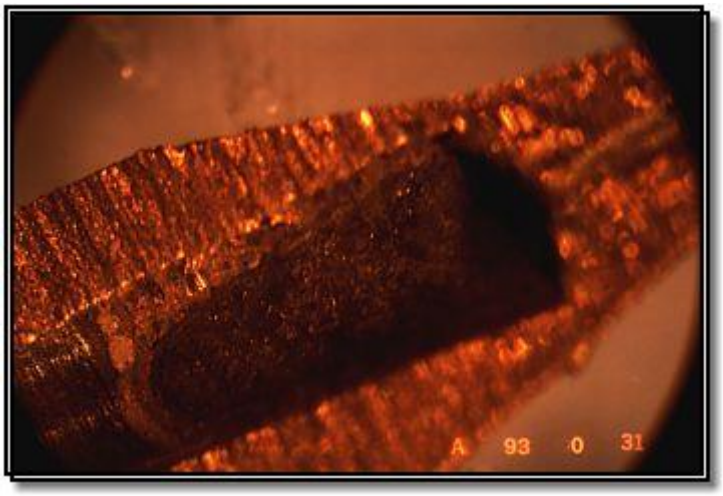
Fotografia nr.13
Repertorio Reinol A-93-0-25
Visualizzazione effettuata mediante stereomicroscopio.
Punta Svizzera di cui alla fotografia nr. 12 a ingrandimento superiore. Si notino le formazioni cristalline anelliformi presenti nella parte posteriore del canalino capillare.

Picture n. 13
Reinol A-93-0-25 Series
The picture was taken from the screen of a stereomicroscope.
Swiss tip already shown in Picture n. 12 at a greater magnification.
Please note the ring-like crystalline formations in the rear part of the inner duct.



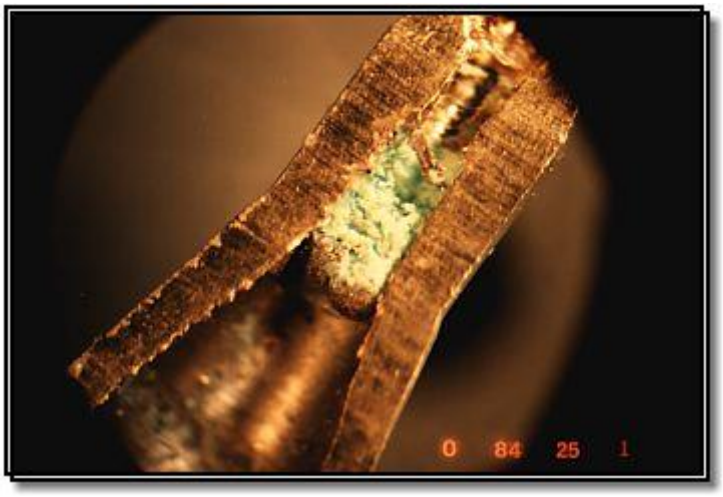
Fotografia nr.14
Repertorio Reinol A-93-0-28
Visualizzazione effettuata mediante stereomicroscopio.
Punta Italiana in cui si può notare come, in questo caso, la corrosione coinvolga l'intera superficie interna in maniera molto evidente.

Picture n. 14
Reinol A-93-0-28 Series
The picture was taken from the screen of a stereomicroscope.
Italian tip were corrosion widely affects the entire inner surface.



Fotografia nr.15
Repertorio Reinol A-93-0-31
Visualizzazione effettuata mediante stereomicroscopio.
Punta proveniente dall'Indonesia.
Notare che il ristagno di liquido nei pressi del canalino capillare retrostante alla sede della sfera ha causato una notevole corrosione acida.

Picture n. 15
Reinol A-93-0-31 Series
The picture was taken from the screen of a stereomicroscope.
Tip coming from Indonesia.
Please notice that the liquid stagnation near the duct behind the ball seat caused a significant saline corrosion.

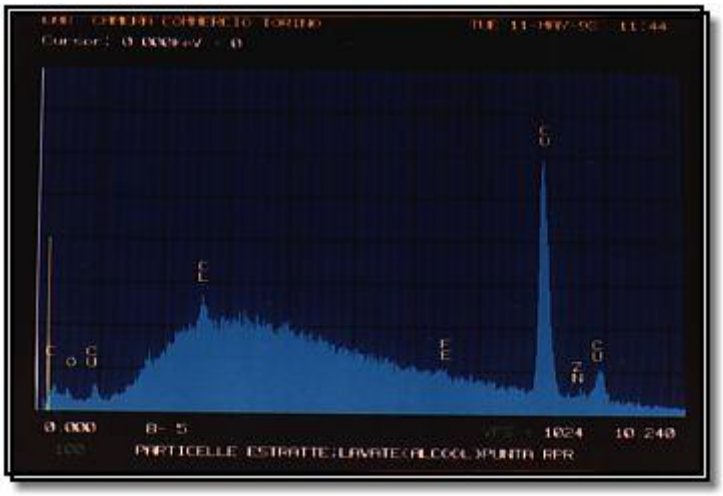


Fotografia nr.16
Repertorio Reinol 0-84-25-1
Visualizzazione effettuata mediante stereomicroscopio.
Punta nichelata al termine della lavorazione.
Esempio di corrosione acida dovuta al trattamento galvanico di nichelatura.

Picture n. 16
Reinol 0-84-25-1 Series
The picture was taken from the screen of a stereomicroscope.
Tip Nickel-plated at the end of the machining process.
Example of acid corrosion due to the nickel-plating galvanic treatment.

Fotografia nr.17
Repertorio Reinol A-93-0
Visualizzazione effettuata mediante stereomicroscopio.
Esempio di punta corrosa dall'acido acetico che si libera dall'idrolisi della resina acetalica (Delrin oppure Hostaform).

Picture n. 17
Reinol A-93-0 Series
The picture was taken from the screen of a stereomicroscope.
Tip corroded by the acetic acid released by hydrolysis of acetalic resin (Delrin or Hostaform)



Fotografia nr.18
Repertorio Reinol-CCIAA
Rappresentazione fotografica dei risultati dell'analisi degli elementi costituenti effettuata al microscopio a scansione elettronica utilizzando uno spettrometro X a dispersione di energia.
Analisi del grumo ceroso presente nell'inchiostro contenuto nella punta di un refill difettoso di cui alle foto nr. 4 e 5.
Si notino i picchi relativi agli elementi costitutivi dell'ottone e quello relativo al cloro. Da notare che il cloro non entra come costituente né nell'ottone né nell'inchiostro ed é quindi presente come inquinante.

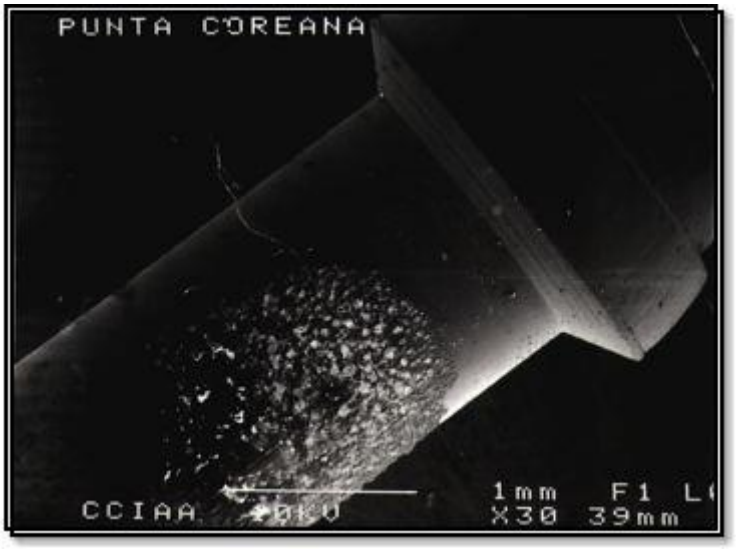
Picture n. 18
Reinol-CCIAA Series
Photographic representation of the findings of a scanning electron microscope observation of elements, using an energy dispersion X spectrometer.
Analysis of the waxy clot found in the ink of a defective refill tip shown in Picture n. 4 and 5.
Please note the peaks of brass and chlorine components. Chlorine is neither part of brass nor of ink, it is therefore present as a pollutant.

Fotografia nr.19
Repertorio Reinol C-92-4
Visualizzazione effettuata mediante stereomicroscopio.
Analisi di una punta nuova dopo immersione in una soluzione 0,1 N di Acido Cloridrico.
Si noti l'evidente corrosione già iniziata dopo appena una settimana dal trattamento.

Picture n. 19
Reinol C-92-4 Series
The picture was taken from the screen of a stereomicroscope.
Analysis of a new tip after dipping into a 0,1 N solution of hydrochloric acid. Please note the visible corrosion already started after a week from treatment.

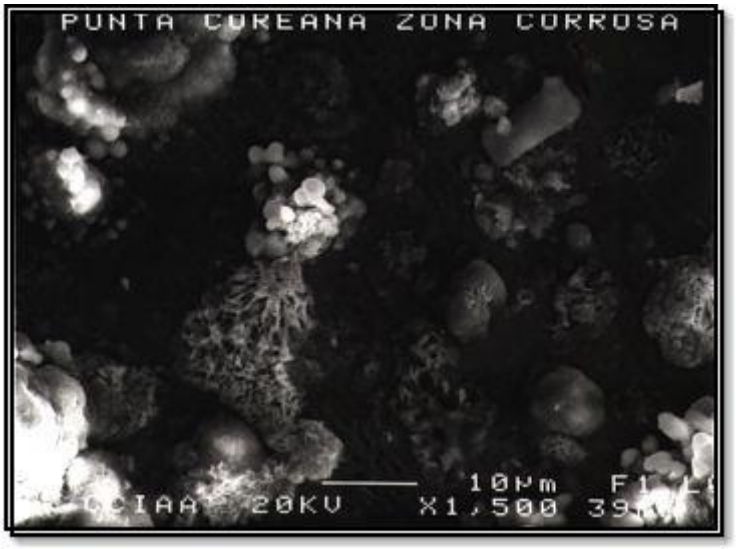
Fotografia nr.20
Repertorio Reinol C-92-5
Visualizzazione effettuata mediante stereomicroscopio.
Analisi della zona anteriore della punta di cui alla foto nr. 19 ad ingrandimento superiore.
Nella zona retrostante alla sede della sfera si può notare la formazione di efflorescenze biancastre che corrispondono perfettamente a quelle presenti nelle punte dei refills difettosi oggetto dell'analisi.

Picture n. 20
Reinol C-92-5 Series
The picture was taken from the screen of a stereomicroscope.
Examination at a greater magnification of the front part of the tip shown in Picture n. 19.
In the area behind the ball you can notice the whitish efflorescence perfectly identical to those present in the tips of defective refills.



Fotografia nr.21
Repertorio Reinol-CCIAA
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 30 X. Parete esterna di una punta Coreana prelevata dallo stesso lotto di produzione di quelle utilizzate per l'assemblaggio dei refills di cui alla foto nr. 2.
Si notino le efflorescenze saline qui molto evidenti grazie alla maggiore profondità di campo data dal microscopio elettronico.

Picture n. 21
Reinol-CCIAA Series
The picture was taken from the screen of a scanning electron microscope using a 30x magnification. Outer wall of a Korean tip taken from the same production lot of those used to assemble the refills shown in Picture n. 2.
Please note the saline efflorescence made more evident by the greater depth of field offered by the electronic microscope.



Fotografia nr.22
Repertorio Reinol-CCIAA
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500 X.
Parete esterna di una punta presentante una notevole zona corrosa di cui alla foto nr.21.
Evidenti sono le efflorescenze saline costituite da sali di Piombo (struttura spugnosa) e Zinco (struttura sferoidale). Le efflorescenze visibili sullo sfondo (poco in rilievo) sono rappresentate da sali di Rame.

Picture n. 22
Reinol-CCIAA Series
The picture was taken from the screen of a scanning electron microscope using a 1.500x magnification.
Outer wall of a tip affected by a conspicuous corrosion shown in Picture n. 21.
There are clearly visible saline efflorescence made of lead (spongy structure) and Zinc (spherical structure) salts. The efflorescence visible in the background is made of Copper salts.

Fotografia nr.23
Repertorio Reinol-CCIAA
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500 X.
Particella estratta da una punta nuova di recente produzione e costituita da sali di Zinco (le formazioni scure a scaglie presenti sullo sfondo rappresentano la struttura cristallina della grafite che viene normalmente utilizzata come supporto).

Picture n. 23
Reinol-CCIAA Series
The picture was taken from the screen of a scanning electron microscope using a 1.500x magnification. Particle extracted from a new recently produced tip made of Zinc salts (the dark flaky formations in the background represent the crystalline structure of the graphite conventionally used as base).

Fotografia nr.24
Repertorio Reinol A-93-0-12
Punta Coreana proveniente da uno dei refills difettosi prelevato dallo stesso lotto di quelli già analizzati nella foto nr. 2.
Notare che dopo l'introduzione dell'inchiostro i cristalli bianchi si colorano e diventa molto difficile una loro attribuzione.

Picture n. 24
Reinol A-93-0-12 Series
Korean tip obtained from one of the defective refills taken from the same lot of those already analysed in Picture n. 2.
Please note that after the introduction of the ink, white crystals become coloured and their analysis becomes more difficult.

Fourth Section
Report of the meeting held on June 4 at the JET HOTEL at Caselle (Turin)
The following companies were present or represented:

We would also like to thank for their presence and collaboration offered during the study:
Mr.Tinazzi, Chemical Engineer of the Chemical Laboratory of the Chamber of Commerce who put at our disposal the scanning electron microscope mentioned several times during this work.
Mr.Beltramino of C.I.A.T. who thanks to his twenty-year experience in the field of chlorinated solvents has given us precious help in the understanding of problems related to the use of halogen derivatives.

Opening speech
(Massimo Gippa - REINOL)
At the beginning of meeting participants were given a warm welcome and thanked for their active participation.
All tests carried out to find out the cause of the defects occurred over the last two years made it clear that the problem could not be solved by our company alone, but that it required the co-operation of all manufacturers. Based on this consideration we decided to summon this meeting - indeed the issue turned out to be far more complex than it was originally thought.
Each participant received a dossier summing up the topics to be dealt with during the meeting (subsequently the dossier formed the basis to draw up this book which is not meant to be a technical manual, nor an exhaustive analysis of all possible issues. It is just intended to become a term of reference for the future, to remember the findings of this work and the way it was communicated to all participants).
the aim of this meeting is not just solving now a problem cropped up in the past and explain its causes. The objective is to lay the basis for a future technical co-operation to prevent the occurrence of new problems that could indiscriminately affect manufacturers of tips, ink and finished products and undermine the image of us all.
We did our best to summon all manufacturers of the items involved in the production process of a pen, since it is only through perfect collaboration that the problem can be totally eradicated.
Many of you , despite your interest in the matter, could not participate because of various reasons, but they will receive a full account of the meeting. The topics and issues examined are both of a toxicological and environmental nature.
Toxicological problems that brought to the elimination of certain products belonging to the production process of ball-point pens.
There are environmental problems too because difficulties in the disposal of manufacturing by-products let to an inappropriate use of the products themselves.
During the opening speech, the opportunity was taken to thank two persons whose work has been essential to advance our research study:
- Mr.Tinazzi (expert in the use of the scanning electron microscope put at our disposal by the Chemical Laboratory of the Chamber of Commerce);
- Mr.Beltramino (who, thanks to his twenty-years experience in the field of chlorinated solvents, was extremely helpful in explaining the problems related to their use).
We divided the meeting into three main topics for discussion:
Mr.Buzzetti started up illustrating the specific issue and the results of tests reported in the first part of this text.
Subsequently, Mr.Tinazzi explained test procedures and will show the first findings.
Finally Mr.Beltramino went into the issue of chlorinated solvents, their properties and the most appropriate way of using them to avoid risks of any kind.
The opening speech was closed expressing the hope that the meeting could be helpful to all of us, not just to collect information on what REINOL discovered, but to promote an exchange of the experiences gathered so far by the different manufacturers.

Problem analysis
(Pietro Buzzetti - REINOL)

The need to carry out a very detailed analysis of the problem and to organise a conference to discuss the results and summon the highest possible number of tips, ink and finished product manufacturers is dictated by the unprecedented nature of the situation.
Since the problem was registered exactly the same way despite the use of materials (tips and inks) supplied by different manufacturers, it was originally felt that the cause had to be searched for in a defective component of the writing instrument.
Right from the start our engineers took into account all possible variables of the production process of defective refills, with special attention to inks; all raw materials used were thoroughly analysed (moreover they were never changed over the last few years). Every single finding of the test confirmed that the cause had to be found elsewhere.
The engineers' work was not easy: a sight analysis of assembled refills was made more difficult by the presence of the dye.
Thanks to the help of the Chemical Laboratory of the Chamber of Commerce and to a fortuitous case, we were able to identify the cause of the writing blocking in a lot of new tips coming from Far East, which already showed macroscopic signs of corrosion.
Mr.Buzzetti went on to describe what is reported in the second section of this text and to show the slides the copies of which are to be found in the third part of this volume.
At the end of his contribution, after mentioning the usefulness of the electronic microscope in our research several times, Mr.Buzzetti asked Mr.Tinazzi (Chemical Engineer of the Chemical Laboratory of the Chamber of Commerce) to illustrate the analysis methodology used and to explain in simple words the operation of the instruments applied during the tests.

Analysis methodology and final results
(Silvio Tinazzi - CCIAA)
Mr.Tinazzi started of f with a description of the research methodology used between January 1992 and June 1993 and briefly showed the instruments applied: a scanning electron microscope JEOL 6400 with a resolution power of about 100 A at 35 Kv and magnification potential up to 300.000x.
The scanning electron microscope (SEM) displays three-D images with a remarkable depth of field. Its monitor does not record primary electrons which would affect the sample being studied and possibly cross it, but the secondary electrons emitted by the sample following the clash of primary electron beams. Moreover secondary electrons, in contrast with primary electrons, are not to be focused but just collected.
Another advantage of this instrument is its wide range of magnification power (you can start from a very low magnification like 10-15x) that provides a more detailed analysis leaving the depth of field unchanged (notice the sharpness of Picture n. 21).
Since each element has a specific emission spectrum, X-ray were used to analyse the various materials. The detection system used in the tests carried out at the Chemical Laboratory of the Chamber of Commerce in Turin consists of an EDS probe (X energy dispersion spectrophotometer TRACOR Z-MAX 30).
With the conventional X-rays detection instruments elements like Carbon, Nitrogen, Oxigen, Fluorine, Litium, cannot be detected. For this reason a NORVAR window has been used through which these elements can pass despite the low energy of their radiations.
This system is made of two plates with a thin silicon-lithium crystal in-between: when an X radiation hits the crystal, its ionises it and generates a current specific to that element.

In the final tests carried our by the Chemical Laboratory of the Chamber of Commerce, tried to verify whether the defects registered up to that moment could be traced back to a single cause, that is the acid corrosion of ball-point pen tips caused by the inappropriate use of chlorinated solvents during washing. Based on this a thorough examination of the following samples was carried out:

- Defective refills. nickel-plated tips and competitors' ink
(Annex D Sample 1)

The tip taken from a defective refill was lightly washed with butanol so as to extract ink without affecting inner parts.

The washed tip was subsequently observed at the electronic microscope with two well-defined landmarks:
- Ball seat (See Picture n. 25);
- Inner wall behind the capillary duct (see Picture n. 26).
The analysis of Picture n. 25 reveals hollow formations and uneven profiles due to a starting corrosion process which becomes even more evident in the inner part of the tip where hollowness is much more visible and widespread (Picture n. 26).

- Artificially polluted Reinol ink (see Annex D samples 2 and 3)

To conform the origin and chemical-physical constitution of this gelatinous mass, we artificially polluted our black ink 101/MG for ball-point pens with Zinc and Copper Chloride.
The ensuing mixture was analysed at the electronic microscope (Picture n. 27 and 28).
Especially in the case of contamination with Copper Chloride, the mass corresponds to the one already observed during previous observations of ink present in defective refills (Picture n. 5 and 30).

- Defective refills: X-10 tips and Reinol ink (see Annex D sample 4).

We first examined the tip to check whether corrosion had already started or not.
The tip taken from a defective refill was lightly washed with butanol so as to extract the ink present without affecting inner walls.
The washed tip was subsequently observed at the electronic microscope with special attention to the part behind the capillary duct that in the previous examination had already yielded the most representative results (see Pictures n. 29).
Here again, the analysis of the walls reveals a clear on-going corrosion process, though less significant and widespread as against the tips of sample n. 1 (point a).
To obtain more accurate results, we also analysed the tip ink content already extracted at the washing stage.
The first microscopic observation showed that the ink mass was not homogeneous, but it had in it a gelatinous area which at a subsequent microscopic analysis (Picture n. 30) revealed the same physical structure detected in previous tests (see Picture n. 5).
We were able to set the constitution of this area thanks to the use of an EDS microprobe (Picture n. 31): the result points to the presence of copper and chlorine causing the gelling of ink.
The chlorine produced through an improper tip washing reacted with copper forming copper chloride. The latter reacts with ink carboxyl and generates carboxylates (metal soap). The final rheology is different from the original one and ink does not flow down smoothly in the duct.
To bear out this theoretical assumption the same analysis was carried out with ink of the same refill but taken from a different area, with no contact with the tip.
In this case the EDS test (see Picture n. 32) did not reveal the typical copper and chlorine peaks, meaning that the two elements are present only inside the tip and not in the original ink formulation.

- Tips treated with hydrochloric acid (see Annex D sample 5).

To make sure that the root cause of all problems was really an acid etching of the tips produced during washing, we decided to reproduce the defect in the laboratory.
1 part of distilled water was mixed with 1 part of Methylene chloride previously extracted from the washing tank of a tip manufacturer.
The mixture thus obtained was shaken, and after the separation of the two solvents, water was used to dampen some good quality defect-free tips.
After 48 hours the tips of that lot were put directly under the electronic microscope to be observed.
Behind the capillary duct (Picture n. 33) you can already see the formation of saline efflorescence (whitish ramifications) which will react to the ink introduced into duct, leaving original sites empty and consequently forming hollow areas.

- Non corroded X-10 tips (Annex D sample 6).

To obtain a further confirmation of this, a new test was performed with tips belonging to a lot of defect-free refills.
In this case there was no corrosion in the ball seat (Picture n.34), and even on the inner wall only rare corrosion sites are to be observed (Picture n.35).

- Corroded X-10 tips (see Annex D sample 7).

To confirm the presence or absence of oxidation in new tips, not yet filled with ink, the electronic microscope was used to observe new tips taken from lots with defective refills.
There are clear signs of corrosion and hollowness both in the ball seat (Picture n.36) and on the wall behind the capillary duct (Picture n.37).
Please note the inappropriate machining of the ink feeding duct; it is obstructed and will not permit a normal ink flow.
There are already numerous crystalline formations of copper and zinc chlorides on the wall behind the inner duct, and if used to assemble refills they will react with ink.
Mr.Tinazzi closed his contribution showing to participants the above-mentioned pictures taken during recent tests.

Introduction to chlorinated solvents
(Beltramino -CIAT)

Mr.Beltramino, who has a twenty-years experience in this specific sector, was invited to the meeting as expert in chlorinated solvents.
He opened his speech with a quick explanation of the main characteristics of chlorinated solvents and how they are industrially obtained.
After a short introduction, he quickly moved to the specific use of these solvents, emphasising the need of their appropriate use - "though stabilised chlorinated solvents are highly unstable".
It is very important to underline that chlorinated solvents, if correctly used and controlled, can yield exceptional results, if they are not properly used however, they can cause a lot of troubles.
The need was stressed to carry out regular checks of washing baths to prevent all the problems mentioned during this discussion.
To explain the remarkable strength of chlorinated solvents, reference was made to the borderline case of a plant manufacturing metal parts that had had serious corrosion problems because washing baths were very close to the production plant.
In that case it was enough to separate the washing department from the manufacturing one to sensitively limit the defect.
Mr.Beltramino moved then to illustrating the most well-known methods to control solvents and detect their acidity. Some of these methods have already been covered before.
The cleaning of the equipment is of paramount importance: the presence of brass powder in the bath may act as catalyst of the decomposition process and increase the acidity of the product.
The presence of oil in the washing bath proportionately increases the solvent boiling temperature. This require an increase in distillation temperature with a consequent greater risk of thermal decomposition.

Attentive use of chlorinated solvents and new washing methodologies
(Rosso - R.P.R. RIGHELLA)

When Mr.Beltramino ended his presentation, Mr.Rosso from R.P.R. (a company manufacturing tips for ball-point pens and refills of various kind), asked all participants to co-operate with Reinol in the future, so as to make it easier to perform tests and detect the cause of possible writing problems.

Mr.Rosso continued his speech asking Mr.Beltramino to explain the reason why such a serious defect has cropped up only very recently even though companies had been using the same working method fro twenty years.
Mr.Beltramino explained that the dismissal of the stabiliser known as 1,4-dioxan had, at least at first, increased the number of problems due to the corrosion of metal parts in every sector of the metal and steel industry.
In the past, the strong stabilisation power of 1,4-dioxan had counterbalanced the effects of inadequate washing.
At this point, Mr.Rosso reply asking for what reason the manufacturers of chlorinated solvents had not let the others know that this stabiliser had been replaced.
According to Mr.Beltramino, not only had these products been presented to all final users, but each manufacturer of chlorinated solvents tends now to emphasise the super-stability of hyper-stability of its solvents.
The owner of R.P.R. himself, who had been informed of the problem a few months before (he had taken part in the final stage of the tests together with Reinol), replaced the old solvent with another one, more suitable to that specific use and is still considering the use of special equipment to vacuum wash his tips (with this method the presence of steam is eliminated because the air re-entered in the machine is previously de-hydrated).

Importance of the equipment used for washing parts
(Claudio Nicol - DIPRO & Pagani - UNIVERSAL)

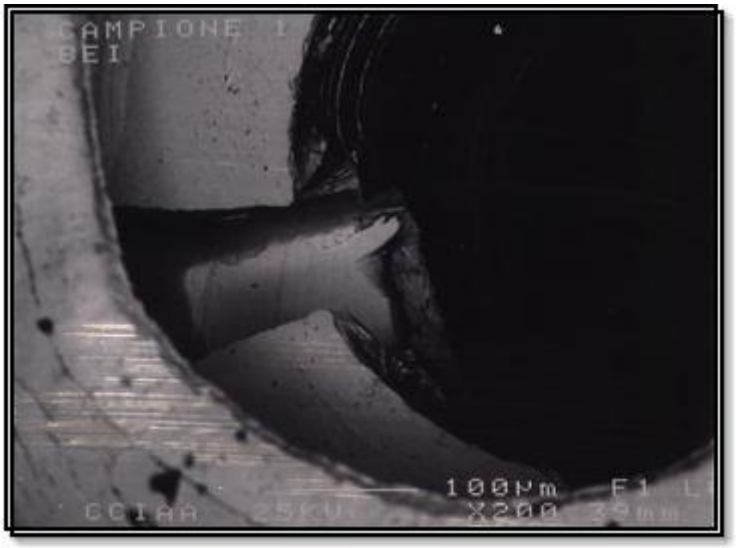
Thanks to a twenty-years experience in the field of washing machines using chlorinated solvents, Dr.Nicol could join to help the audience understand the issue better.
In his opinion, it is unthinkable that in certain companies the problems under study do not occur, since the use of chlorinated solvents is often inappropriate and the equipment, in most cases, unsuitable.
It is very important to update machines and equipments with necessary modifications, so as to limit as much as possible the thermal shock to which every solvent is subjected during heating stage.
He further recommended to avoid heating the solvent with heating elements that are the main cause of thermal decomposition.
to demonstrate this, he gave the example of washing machines for garments where the solvent was directly heated with heating elements. The latter became corroded and unusable in very short time. By contrast, heating carried out with steam coils, ensured a longer life of the equipment (even as long as ten years) manufactured in zinc-plated steel at the time.
Here again the pH control play a very important role.
Based on his personal experience, Dr.Nicol advised against the used of vacuum plants: results do not seem to live up to the expectations, especially with respect to separation at the aqueous stage.
This was also confirmed by Mr.Pagani of Universal. He also recommended to try and avoid the presence of water when working in total absence of thermal shocks.

Corrosion of machined but unwashed parts
(Christophe Dumusois - HAUSER)

The very interesting contribution by Mr.Dumusois stressed that Hauser too performed studies on the corrosion of roller tips.
The question was raised how can corrosion attack tips machined without using oil, unwashed and, what is more surprising, attack the un-machined part of the tip.
Mr.Buzzetti with the support of Mr.Rosso explained that over his latest visit to Boillat (manufacturer of brass bars), these problems had been touched upon. Apparently the manufacturers of brass themselves carry out the pickling of brass bars using chlorinated solvents (at the end of the extrusion process).
The reason why Mr.Dumusois observed corrosion in an un-machined part of the tip can be easily explained. In this case corrosion started at the brass bar manufacturing stage already.

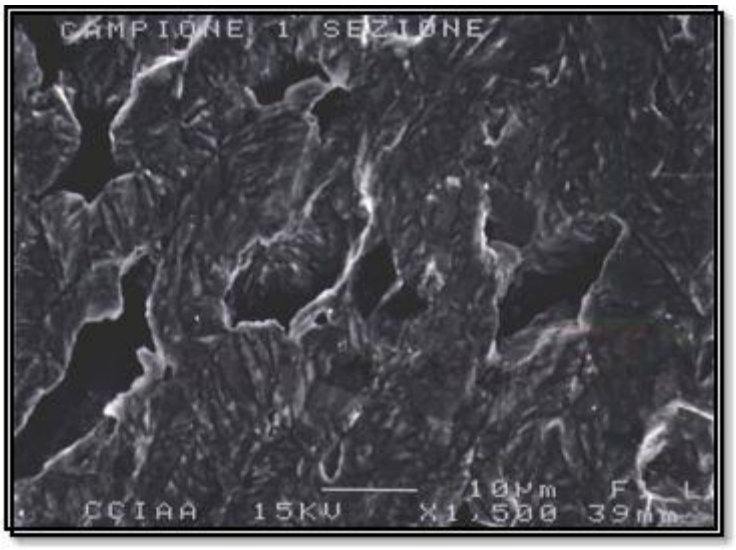
Can the ink pH play an important role in corrosion ?
(Mr.Santini - Premec)

At this point Mr.Santini raised a very interesting question: can the ink pH play an important role in corrosion ?.
He pointed out that among German manufacturers there are two schools of thought in the formulation on ink fro ball-point pens: one prefers inks with an acid pH, the other a neutral or slightly alkaline pH.
Mr.Buzzetti replied that Reinol is familiar with both options and, in fact, it adopts both for the following reasons.
Many years ago tips were obtained from a brass tube by pressing. Brass used have a very high copper content, therefore inks with an acid pH were very good, whereas inks with a neutral or slightly alkaline pH had a limited shelf-life, a year approximately. In some cases neutral or alkaline inks yielded the best results, for instance when using tip manufactured in aluminium alloys.
Now both inks are being produced, but with corroded tips they raise the same problems.
Moreover the same defects have been registered in refills with ink formulated according to both theories.



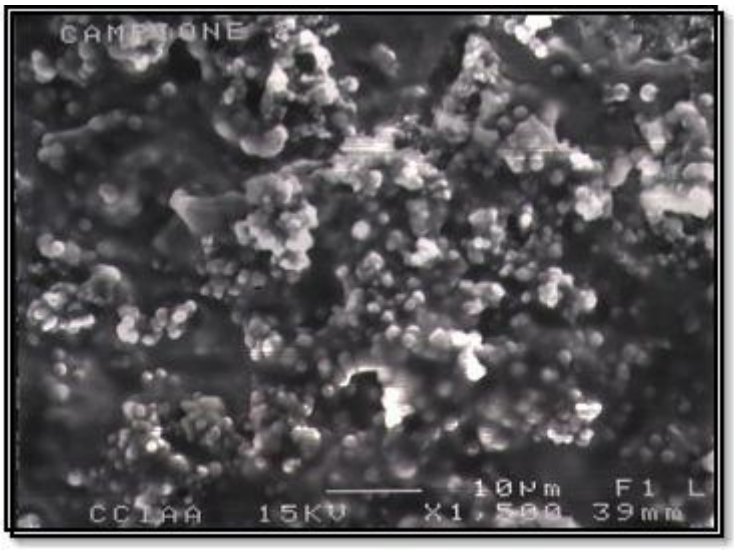
Fotografia nr.25
Repertorio Reinol-CCIAA
Campione 1
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 200x. Sede sfera di una punta prelevata da un refill difettoso contenente inchiostro della concorrenza. Si notino le cavernosità presenti sulle pareti del canalino di alimentazione dell'inchiostro e le piccole vaiolature presenti sui piani della punta.

Picture n. 25
Reinol-CCIAA Series
Sample 1
The picture was taken from the screen of a scanning electron microscope with a x200 magnification. Ball seat of a tip taken from a defective refill holding competition ink. Please note the hollowness on the walls of the ink feeding duct and the slight pitting on the tip surface.



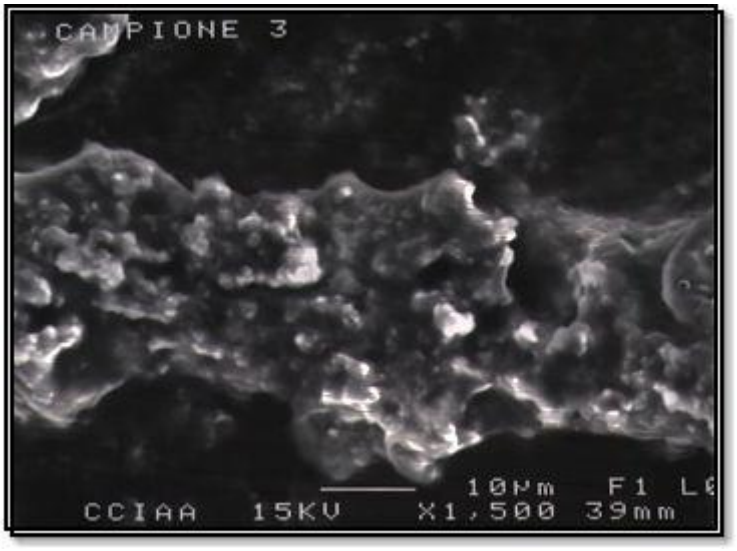
Fotografia nr.26
Repertorio Reinol-CCIAA
Campione 1
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500x. Parete interna di una punta prelevata da un refill difettoso contenente inchiostro della concorrenza. In questo caso si può vedere come il fenomeno di corrosione ha alterato totalmente la struttura del metallo.

Picture n. 26
Reinol-CCIAA Series
Sample 1
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification. Inner wall of a tip taken from a defective refill holding competition ink. Here you can see how corrosion totally altered the metal structure.



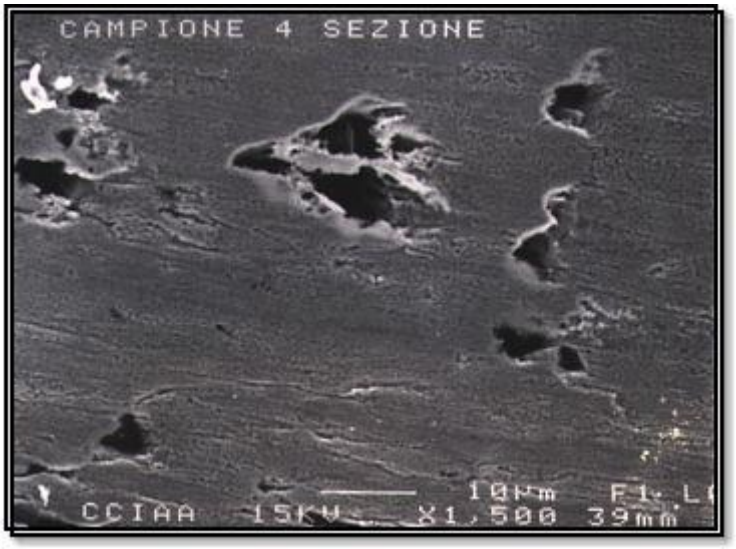
Fotografia nr.27
Repertorio Reinol-CCIAA
Campione 2
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500x.
Analisi del grumo di consistenza cerosa proveniente da un'inquinamento dell'inchiostro ricreato in laboratorio utilizzando cloruro di rame.

Picture n. 27
Reinol-CCIAA Series
Sample 2
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification.
Analysis of the waxy clot produced by the artificial contamination of ink with copper chloride.



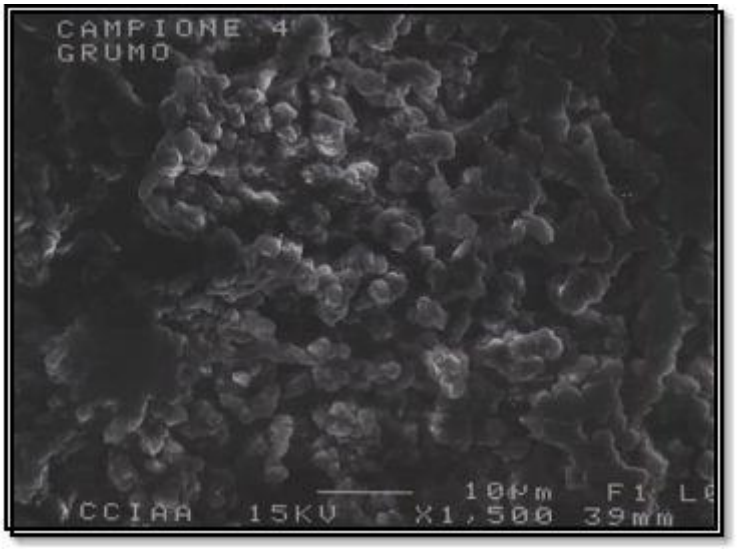
Fotografia nr.28
Repertorio Reinol-CCIAA
Campione 3
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500x.
Analisi del grumo di consistenza cerosa proveniente da un'inquinamento dell'inchiostro ricreato in laboratorio utilizzando cloruro di zinco.

Picture n. 28
Reinol-CCIAA Series
Sample 3
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification.
Analysis of the waxy clot produced by the artificial contamination of ink with zinc chloride.



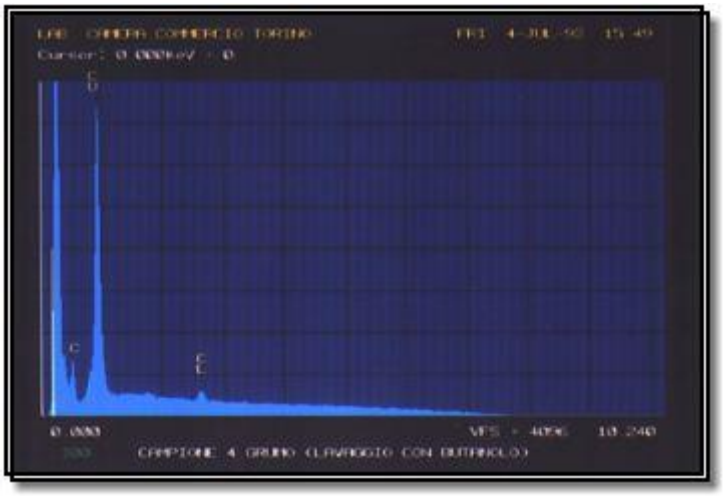
Fotografia nr.29
Repertorio Reinol-CCIAA
Campione 4
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500x.
Parete interna di una punta prelevata da un refill difettoso contenente inchiostro Reinol.
Notare, confrontando con la fotografia nr.26, la minore presenza di cavernosità (seppure presente) e la totale assenza delle vaiolature.

Picture n. 29
Reinol-CCIAA Series
Sample 4
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification. Inner wall of a tip removed from a defective refill with Reinol ink. Please compare this picture with picture n. 26 and note the smaller hollowness (though present) and the complete absence of pitting.



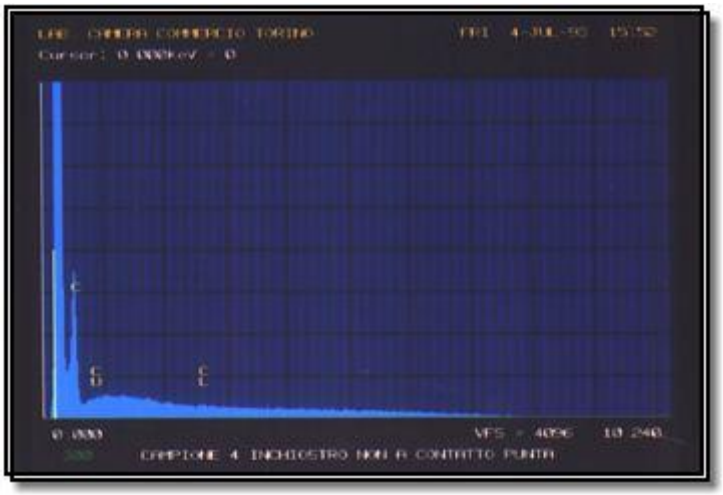
Fotografia nr.30
Repertorio Reinol-CCIAA
Campione 4
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500 X.
Analisi del grumo di consistenza cerosa presente nell'inchiostro contenuto nella punta di un refill difettoso di cui alla foto nr.29.
Notare la struttura cristallina a elementi sferoidali delle particelle contenute nella massa in analisi.

Picture n. 30
Reinol-CCIAA Series
Sample 4
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification.
Analysis of the waxy clot of ink held in the tip of a defective refill shown in Picture n. 29.
Please note the spherical crystalline structure of the mass particles.



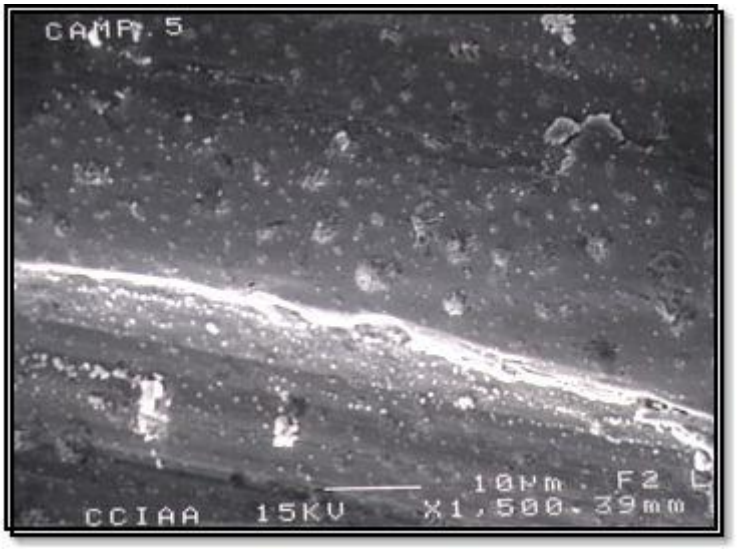
Fotografia nr.31
Repertorio Reinol-CCIAA
Campione 4
Rappresentazione fotografica dei risultati dell'analisi degli elementi costituenti effettuata al microscopio a scansione elettronica utilizzando uno spettrometro X a dispersione di energia.
Analisi del grumo di consistenza cerosa presente nell'inchiostro contenuto nella punta di un refill difettoso di cui alle foto nr. 29 e 30. Si notino i picchi relativi al Rame ed al Cloro.

Picture n. 31
Reinol-CCIAA Series
Photographic representation of the analysis of constituents obtained with a scanning electron microscope and an X energy dispersion spectrometer.
Analysis of the waxy clot of ink held in the tip of a defective refill shown in Pictures n.29 and 30.
Please note the copper and chlorine peaks.



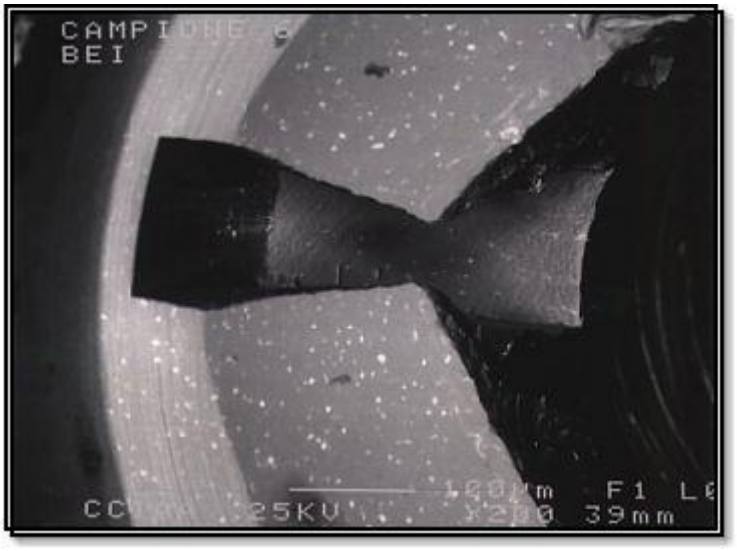
Fotografia nr.32
Repertorio Reinol-CCIAA
Campione 4
Rappresentazione fotografica dei risultati dell'analisi degli elementi costituenti effettuata al microscopio a scansione elettronica utilizzando uno spettrometro X a dispersione di energia.
Analisi del grumo ceroso presente nell'inchiostro contenuto in un refill difettoso prelevato in una zona non a contatto con la punta (vedi foto nr.31). In questo caso i picchi relativi al Rame ed al Cloro non sono presenti segno evidente che non fanno parte della normale formulazione dell'inchiostro.

Picture n. 32
Reinol-CCIAA Series
Photographic representation of the analysis of constituents obtained with a scanning electron microscope and an X energy dispersion spectrometer.
Analysis of the waxy clot of ink held in the tip of a defective refill and taken from an area not in contact with the tip. In this case copper and chlorine peaks are absent (see picture n.31), meaning they do not stem from the ink.



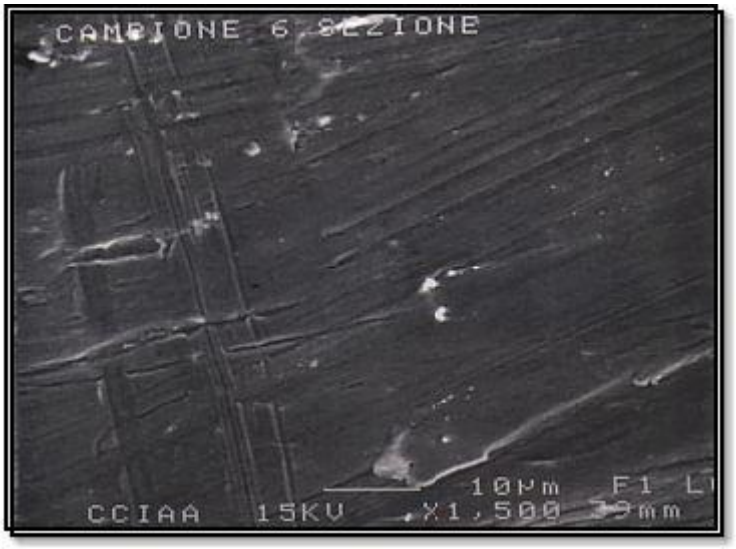
Fotografia nr.33
Repertorio Reinol-CCIAA
Campione 5
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500 x.
Parete interna di una punta nuova in cui si é riprodotto il fenomeno di corrosione dovuta ad attacco acido come già descritto in precedenza.
Si notino le già evidenti efflorescenze saline biancastre che verranno in seguito asportate dall'inchiostro provocando la formazione delle ben note cavernosità.

Picture n. 33
Reinol-CCIAA Series
Sample 5
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification. Inner wall of a new tip where corrosion due to acid etching has been reproduced following the description previously mentioned.
Please note the evident whitish saline efflorescence subsequently removed from the ink and causing the well-known hollow formations.



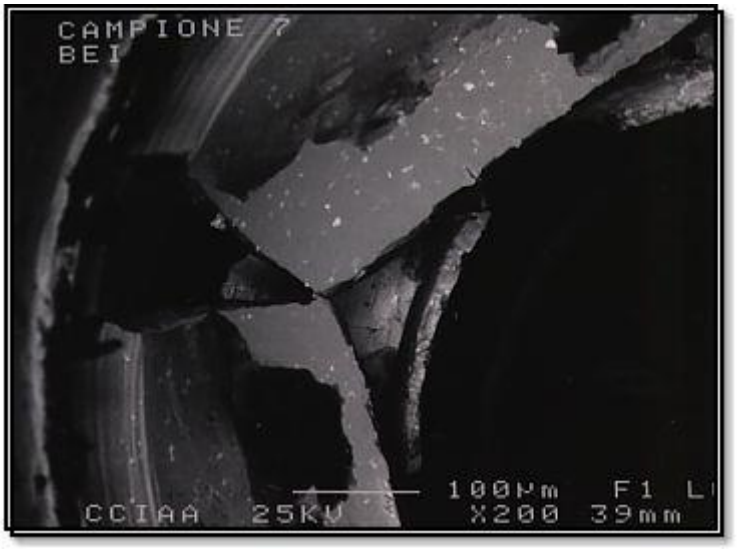
Fotografia nr.34
Repertorio Reinol-CCIAA
Campione 6
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 200x. Sede sfera di una punta sana proveniente da un lotto non presentante il difetto. Si noti la totale assenza di cavernosità dovute a fenomeni corrosive.

Picture n. 34
Reinol-CCIAA Series
Sample 6
The picture was taken from the screen of a scanning electron microscope with a x200 magnification. Ball seat of a tip picked from a defect-free lot. Please note the complete absence of hollowness due to corrosion.



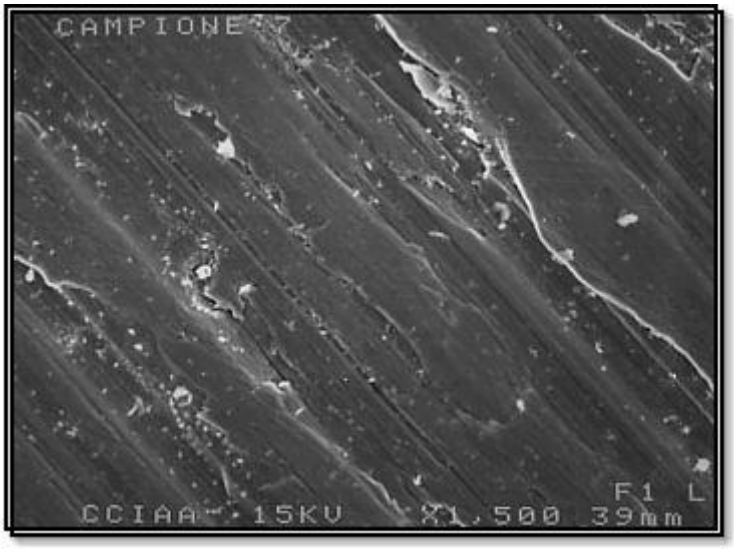
Fotografia nr.35
Repertorio Reinol-CCIAA
Campione 6
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500x. Parete interna di una punta sana proveniente da un lotto non presentante il difetto. Il campione presenta radi focolai di corrosione.

Picture n. 35
Reinol-CCIAA Series
Sample 6
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification. Inner wall of a non corroded tip picked from a defect-free lot. The sample shows rare sites of corrosion.



Fotografia nr.36
Repertorio Reinol-CCIAA
Campione 7
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 200x. Sede sfera di una punta X-10 nuova proveniente da un lotto presentante il difetto. Si noti la notevole irregolarità delle superfici interne dovuta al fenomeno di corrosione ormai in stadio avanzato.

Picture n. 36
Reinol-CCIAA Series
Sample 7
The picture was taken from the screen of a scanning electron microscope with a x200 magnification. Ball seat of a new X-10 tip picked from a defective lot. Please note the unevenness of inner surfaces due to an advanced corrosion stage.



Fotografia nr.37
Repertorio Reinol-CCIAA
Campione 7
Visualizzazione effettuata mediante microscopio a scansione elettronica utilizzando un ingrandimento di 1.500x. Parete interna di una punta X-10 nuova proveniente da un lotto presentante il difetto. Il campione presenta evidenti focolai di corrosione.

Picture n. 37
Reinol-CCIAA Series
Sample 7
The picture was taken from the screen of a scanning electron microscope with a x1.500 magnification. Inner wall of a new X-10 tip picked from a defective lot. The sample shows evident sites of corrosion.

Conclusion
At the end of the meeting Reinol stated that a number of customers showed interest in the setting up of a centralised laboratory specialised in research and study of these issues and in products quality control.
To meet this need, Reinol suggested to utilise an already existing structure with highly qualified personnel specialised in this sector and made its own laboratory available.