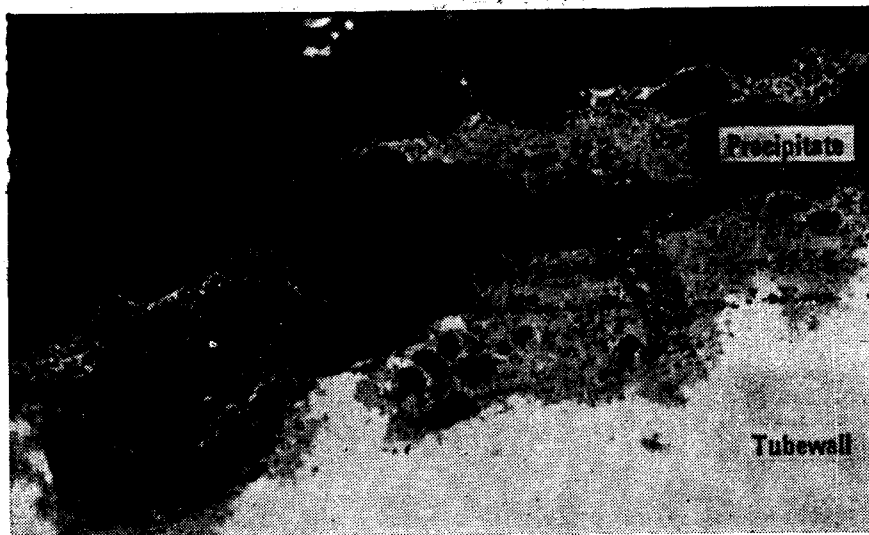


Boiler Water Treatment with Polyamines

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Transverse section of economizer tube with magnetite-hematite deposits after long period of use with conventional water treatment program (80x).

Like water in boilers and closed hot water systems, condensate in steam systems generally contains carbon dioxide and, not infrequently, oxygen. This leads to corrosion of parts of the system exposed to water and steam—both acid corrosion due to low pH in the carbon dioxide-water system and oxide formation due to the presence of oxygen. Moreover, corrosion problems can be caused by galvanic effects in systems of dissimilar metals (e.g. heat exchangers). Precipitation of corrosion products and salts in the systems leads to impaired performance. A previous article (1) dealt with problems in boiler water systems as a result of precipitations and deposits, corrosion, foaming etc as well as possible remedies.

Traditional treatment programs to counteract corrosion and precipitations in boiler water systems may include additions to the feed water of sodium hydroxide, trisodium phosphate, ammonia, hydrazine, sulphite, polyacrylate etc besides softening with ion exchangers of condensate and feed water (cf ref 1). This type of treatment program can be completely replaced today by additions of aminopolyamine-based multi-purpose products.

Neutralizing amines

Volatile amines such as morpholine, cyclohexylamine, dicyclohexylamine, benzylamine and amino alcohols such as diethylamine methanol, amino butanol etc have been used for the neutralization of carbon dioxide/carbonic acid in e.g. condensate since the mid-1950s (2—4). In contrast to ammonia, the use of volatile amines does not, as a rule, entail any problems with copper corrosion. In particular, mixtures of volatile amines with different vapour pressures and distribution coefficients for water-vapour phase are used, which permits an amine transport with subsequent carbon dioxide neutralization to parts of a large steam-condensate system with widely differing pressure temperature conditions. At 350—400°C, a degradation of e.g. morpholine and cyclohexylamine to ammonia, among other products, takes place, which also has a neutralizing effect. However, the volatile amines

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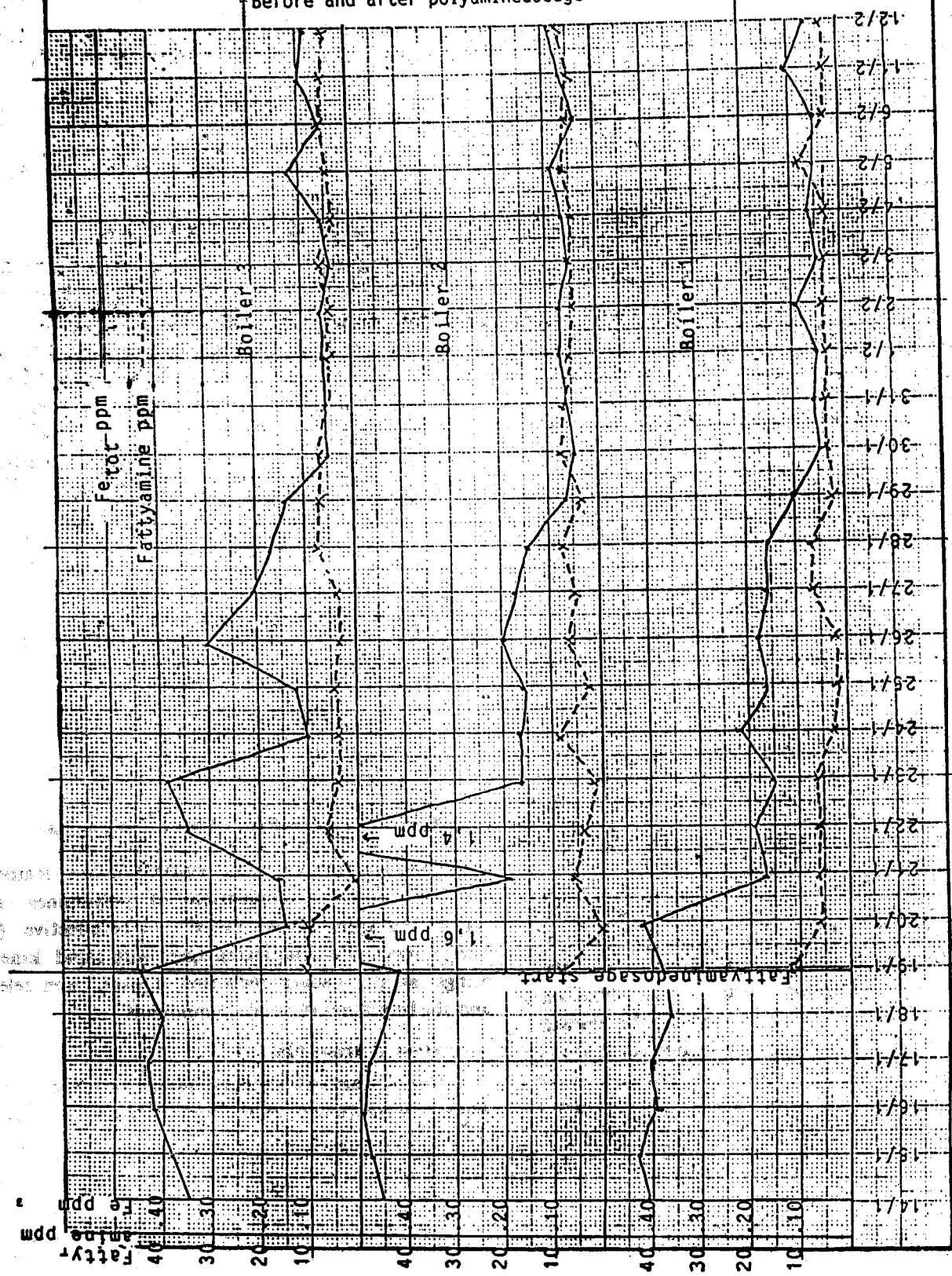
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SSAB
Oxelösund

Iron and fattyamine content in boiler-
water P1, P2 and P3 at SSAB-OK2
Oxelösund Sweden.
Before and after polyaminedosage

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provide no protection against corrosion caused by gaseous oxygen in the water. At high carbon dioxide levels and strong amine concentrations, a precipitation of carbonates can some times take place.

Film-forming

aliphatic monoamines

Aliphatic primary monoamines of the type $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$, $n=10-20$, were developed during the early 1950s (5,6). Typical products are dodecylamine ($n=11$), hexadecylamine ($n=15$), octadecylamine ($n=17$), etc., but primary amines with branched carbon chains as well as secondary amines have also been tried. These amines are relatively non-volatile and do not have a carbon dioxide-neutralizing effect. Instead, they form an adhesive, normally monomolecular film (with a thickness in the neighbourhood of 10Å) on water-exposed surfaces with the hydrophilic N group towards the metal. The hydrophobic hydrocarbon chain prevents wetting of the metal surface. Film coverage is dependent on the strength of the metal-nitrogen bond, but also on the shape, orientation and length of the carbon chain. Optimal film formation seems to occur for straight chains with a length of 10 to 18 carbon atoms. Products with these chain lengths possess low solubility in water, and a combined dosage with a dispersant is required.

Aliphatic monoamines are effective inhibitors already at substoichiometric concentrations and provide good protection in clean, new systems. On the other hand, they provide poor protection on surfaces where substantial corrosion has already occurred. Loosely adhering corrosion products can be dislodged and can also initiate polymerization of the product under certain conditions. High flow, especially in combination with the presence of solid particles, can easily destroy the amine film.

Film forming aliphatic polyamines

Polyamines with a composition of the type $\text{CH}_3(\text{CH}_2)_n\text{NH}[(\text{CH}_2)_3\text{NH}]_x(\text{CH}_2)_3\text{NH}_2$, $n=11-17, x=3-5$, were developed in the early 1960s (7-9). Like the monoamines, the polyamines form adhesive films on clean metallic surfaces and prevent even the growth of microcrystalline calcium and magnesium salts. However, the monomolecular surface film is more adhesive and has better coverage than the equivalent monoamine film due to the fact that all nitrogen atoms can be

bound to the metal, Figure 1, with considerably better corrosion protection as a result. A chelate-like (C_3N_3) (metal) bond has even been suggested for polyamines (7).

The polyamines are stable within a wide range of temperatures up to 500°C in the vapour phase and can be used at working pressures of up to 10 MPa. Long-term testing at 305°C, 10 MPa and a thermal load of 15 MJ/m²,h has not indicated any deterioration of function (10). The active pH range is 4-9 and above. As in the case of the aliphatic monoamines, surface films only form in connection with condensation in water-exposed parts of the system, and not in only steam-exposed parts.

Polyamine-based multi-component mixtures

Combinations of aliphatic film-forming monoamines and volatile neutralizing amines have been used successfully since the mid-1960s. Polyamine-based commercial products also contain volatile neutralizing amines and dispersants and hence provide effective corrosion protection in both water and steam-exposed parts of the system, against both acid attack and corrosion resulting from residual oxygen. Additional treatment with dispersants for precipitation control is unnecessary.

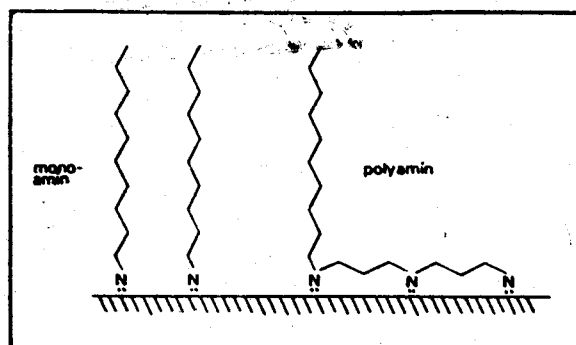


Figure 1. The function of film-forming amines.

Especially for hot water systems at low temperatures (< 120°C), combinations of polyamines and complexing agents have proven to be effective (8). The presence of a complexing agent with rapid kinetics brings about a sharp reduction of both iron release and the formation of solid compounds.

Formation of amine film

Unifos Kemi AB in Stenungsund switched in 1981 from a conventional boiler water treatment program (15-20 ppm trisodium phosphate, 75 ppm polyacrylate-

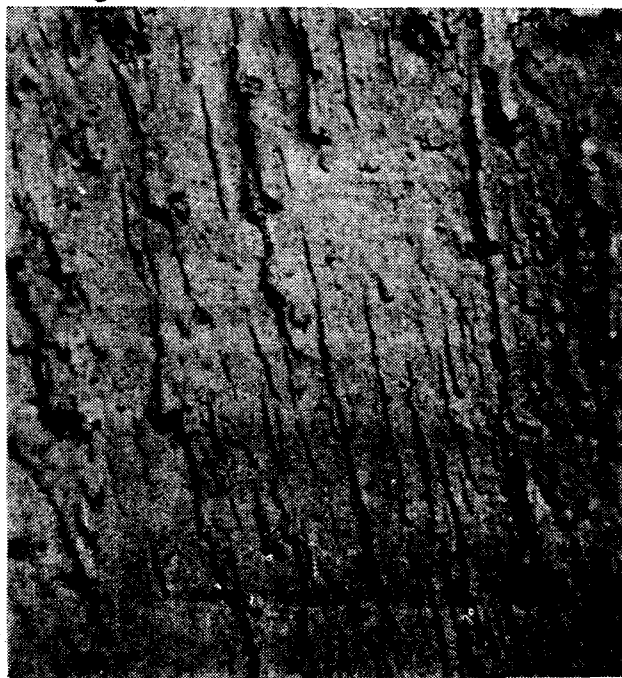


Figure 2 Longitudinal section economizer tube with magnetite-hematite deposits after long period of use with conventional water treatment program.

based dispersant, 10 ppm hydrazine) to a treatment with a polyamine-based product that was continuously charged to the feed water to a concentration corresponding to 20-30 ppm to compensate for the make-up water supply. Samples were taken from economizer tubes prior to the changeover to the polyamine program and after three months of polyamine treatment, and the precipitation products on water-exposed surfaces were examined with SEM (scanning electron microscopy), ESCA (electron spectroscopy for chemical analysis) and SIMS (secondary ion mass spectrometry) (11).

Prior to the changeover to the polyamine program, the economizer surfaces were covered with a 0.2–0.6 mm thick layer consisting chiefly of magnetite. After three months of polyamine treatment, there was still a thin magnetite film 0.04–0.08 mm thick (cf. Figure 2). No signs of increased corrosion could be observed in a newly-installed tube section. Both the ESCA and SIMS examinations revealed that a thin film containing amine nitrogen had formed on the exposed metallic surfaces (cf. Figure 3–5) (11).

Case histories

Steam system at petrochemical plant. In a steam system

of the traditional type (Eckrohr boiler, working pressure 2.7 MPa, steam production 100 t/h, condensate return 70%) (12) with raw water from a lake, sodium hydroxide, trisodium phosphate hydrazine and polyacrylate were added to the feed water. No special conditioning of the condensate water was carried out. A changeover was made to addition of a single multi-component polyamine product. Despite

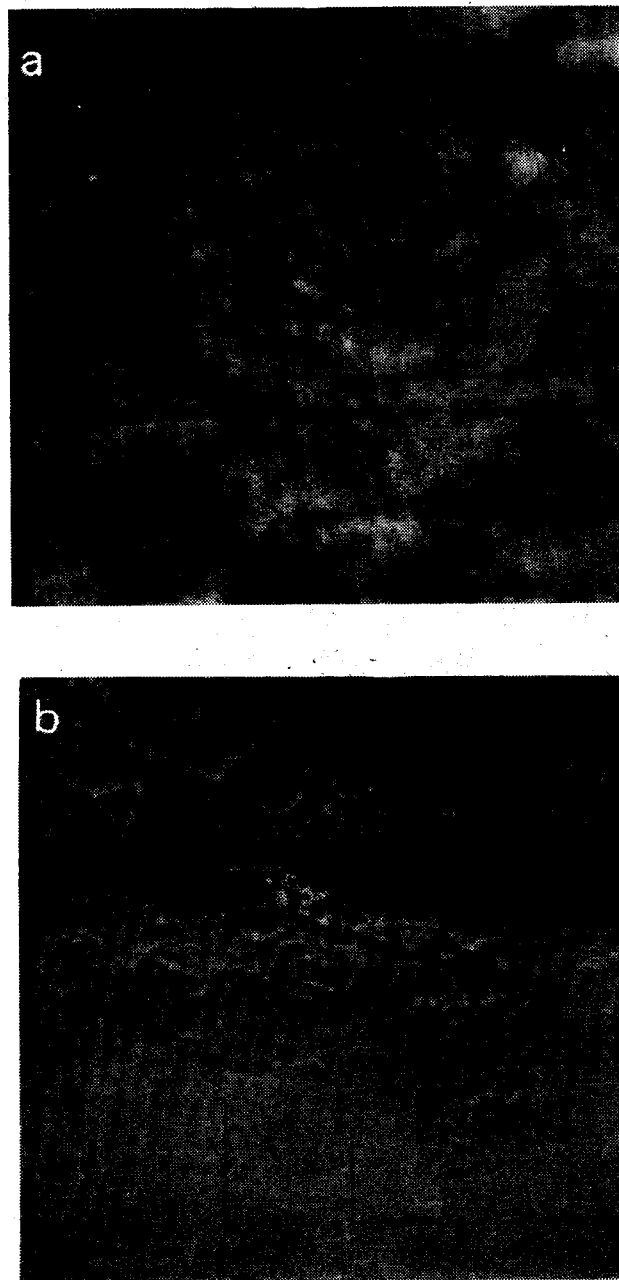


Figure 3. SEM micrographs of tube surface after polyamine treatment (1000x).

(a) Surface structure (b) Cross section

discontinuation of sodium hydroxide charging, a high pH was maintained both in the feed water (unchanged at about 9.5) and in the boiler water (drop from about 11.5 to about 11.2). In the condensate water the pH was increased (from about 8.5 to about 9.5) as a result of the volatile amines. An insignificant reduction of conductivity was observed, while the iron level fell from 0.2-0.4 mg/l (max 0.9 mg/l) to less than 0.05 mg/l after a month or so. Since the changover to the polyamine program, the degassing pressure and bottom blowing have been reduced.

Boilers at pulp mill. In the soda recovery boilers and steam boilers (2 of each) at a pulp mill (13) (working pressure about 6 MPa, steam production 65, 130, 30 and 30 t/h, steam-temperature after superheater about 450°C, feed water temperature 115°, condensate return about 75, make up water (deionized) about 2000m³/d), a change over was made from a conventional treatment program (trisodium phosphate, polyacrylate, hydrazine etc) to a polyamine program. A high pH was maintained both in the boiler water (9.0-10.0) and in the steam (increase from 8.5-9.2 to 9.2-9.6). Some reduction of conductivity was noted, plus a considerable reduction of the iron level (from 1.0-1.4 mg/l to less than 0.05 mg/l in one of the soda recovery boilers). After changeover to the polyamine program, bottom blowing was reduced to less than 0.1% of steam production. No negative effects such as increased corrosion or sludge formation, or reduced output of the turbine, which had previously been noted during the conventional treatment — were obtained after changeover to the polyamine program.

Conclusions

In most steam and hot water systems and closed cooling

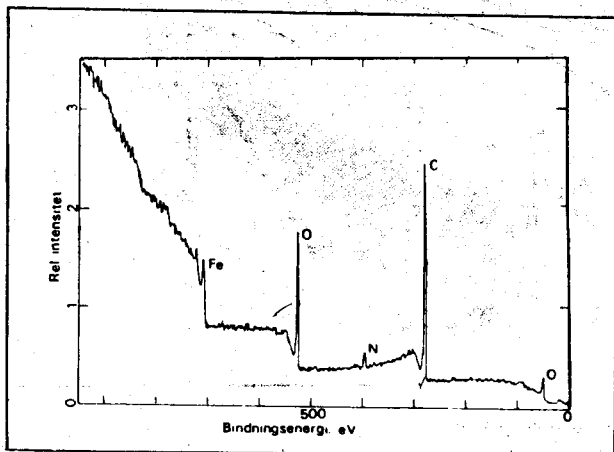


Figure 4. ESCA spectrum of precipitation of tube surface after polyamine treatment.

water systems, traditional conditioning programs can be replaced by treatment with polyamine-based multi-component products (polyamine + volatile amine + complexing agent and dispersant).

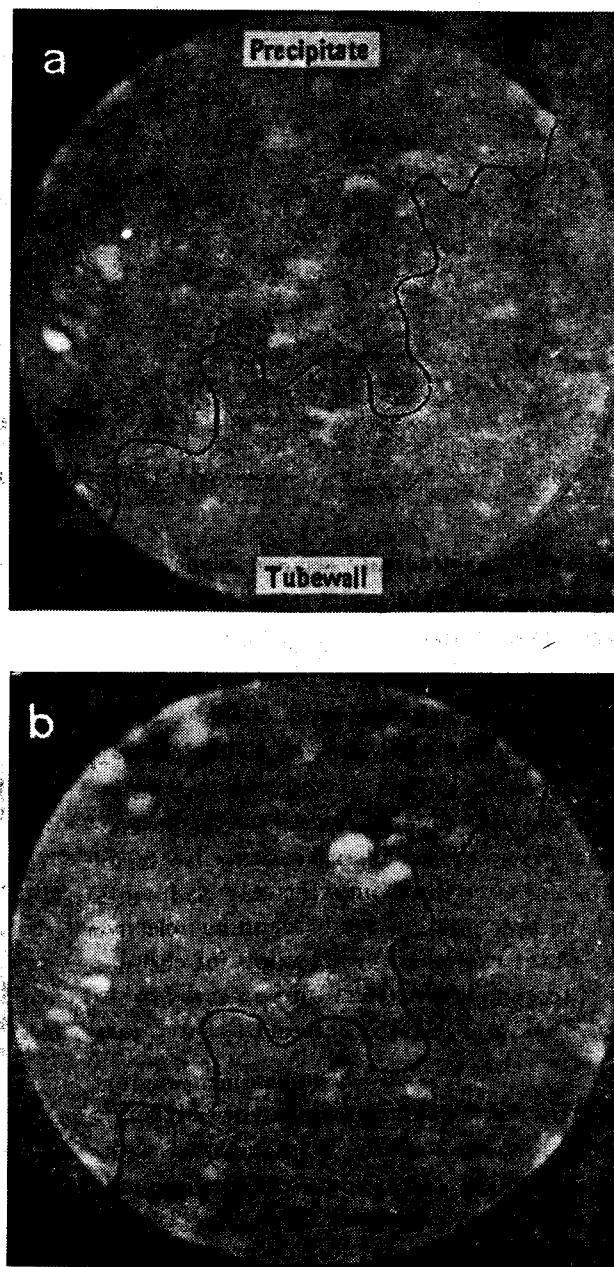


Figure 5. SIMS images on precipitation on tube surface after polyamine treatment (cross section, 320x).

- (a) Carbon-carbon; light areas indicate presence of carbon.
- (b) Carbon-nitrogen; difference in light areas between a and b indicates presence of nitrogen.

Such product mixes afford

- * good corrosion protection through formation of adhesive films on water-wetted metallic surfaces
- * good neutralization of carbon dioxide and pH control in all parts
- * dispersion of precipitation products
- * reduced salt addition
- * simple handling of non-toxic products.

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