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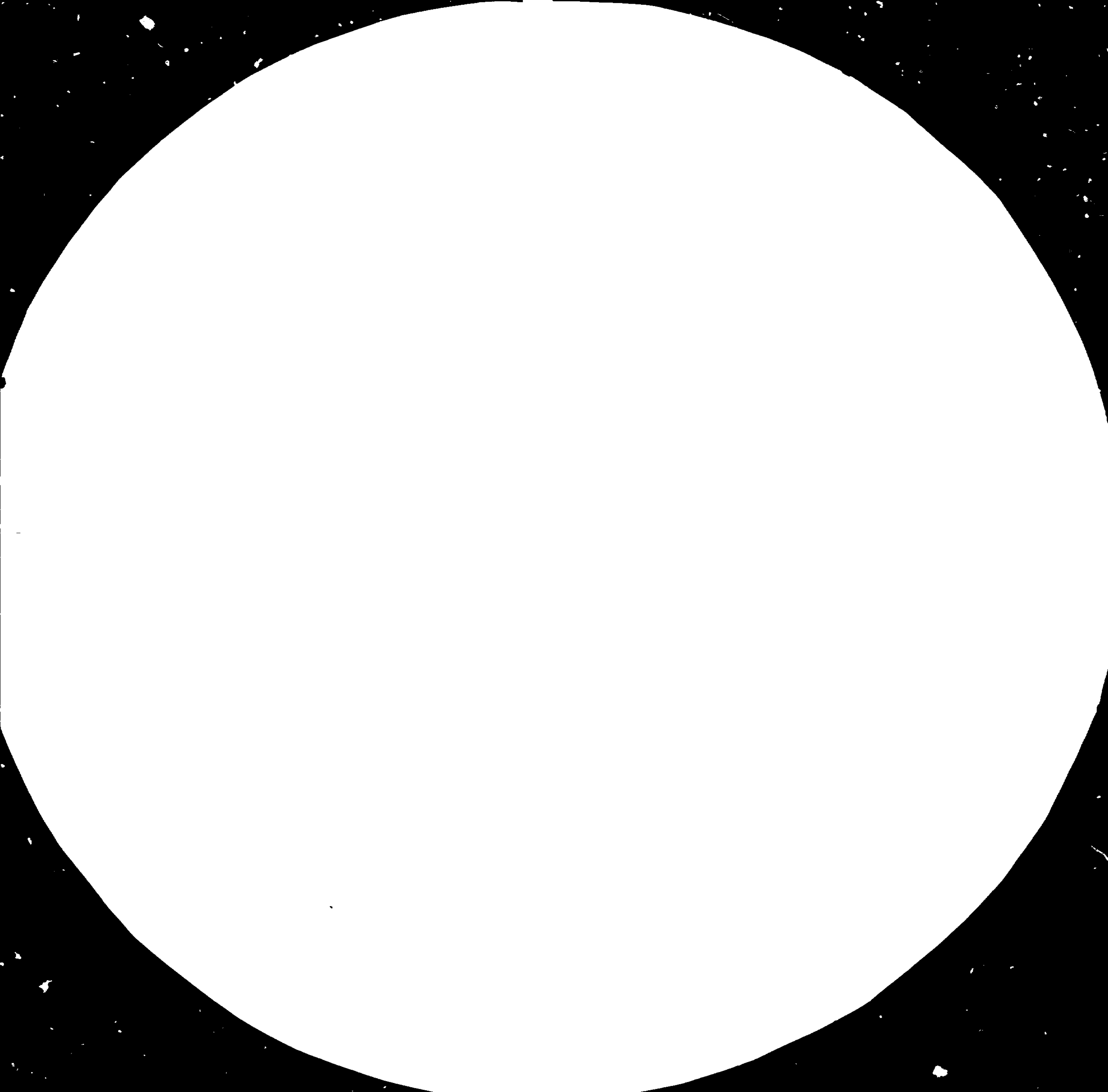

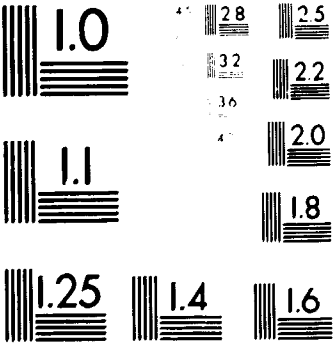

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

14581

March 1985

REPORT FOR

PROJECT SI/ROM/84/801/11-01

Romania.

ANTICORROSIVE PROTECTION MATERIALS MANUFACTURED FROM INDIGENEOUS RAW MATERIALS USED IN THE ARTIFICIAL FIBRE INDUSTRY

Based on the work of DR. REINHOLD STENNER

UNIDO Consultant in the Manufacture of Anticorrosive
Protection Materials for the Viscose Artificial
Fibre Industry (First Part Split Mission - One Week)

3391

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

VIENNA

Consultant in the Manufacture of Anticorrosive Protection Material for the Viscose Artificial Fibre Industry

Report on visit to the Braila artificial fibre factory and discussion with Messrs. Cupsik, Bucarest, 15 - 19 January 1985

1. General remarks

In the Braila artificial fibre factory, artificial silk, staple fibres (short and long fibres) and film are produced from cellulose via viscose and xanthate. CFA Braila is the largest artificial fibre factory in Romania and produces about 80 per cent of Romanian requirements.

2. Brief description of the process

2.1 Cellulose is converted to alkaline cellulose with a caustic soda solution (NaCH). This alkaline cellulose is separated by pressing and ripened. These processes take place in an alkaline medium, so that there is no corrosion, for which reasons normal steel tanks are used.

2.2 The flocculent alkaline cellulose is converted (sulphided) with carbon disulphide (CS_2), caustic soda solution being used as the solvent. Viscose is formed in the process. This stage of the reaction also takes place in an alkaline medium, so that no danger of corrosion arises and normal steel tanks can be used.

2.3 The viscose is ripened for 24 to 48 hours in normal steel tanks, is then degassed and filtered in a filter press using filter plates. As a result of the rinsing processes and the presence of oxygen, corrosion of normal steel can take place at this stage. For that reason, either the normal steel must be protected by coating with rubber or special steel tanks are used, the most satisfactory procedure being to use X10CrNiTi18/9 special steel according to DIN 4541. The filter plates can be of rubber-coated normal steel, though polypropylene is better.

2.4 The viscose is degassed and spun in a so-called Müller bath. The composition of the bath is as follows:

7 - 12% sulphuric acid (H_2SO_4);
16 - 23% Glauber's salt (Na_2SO_4);
1 - 6% zinc magnesium - ammonium sulphate.

On extrusion into the Müller bath, two processes take place simultaneously: the coagulation of the cellulose xanthate and the hydrolytic decomposition of cellulose with the re-formation of carbon disulphide and the formation of Glauber's salt. Hydrogen sulphide and elemental sulphur are formed as by-products. The spinning and precipitating bath is operated and prepared on the circulation principle.

This entire stage of the process is highly corrosive, because of the high temperature and high concentration of sulphuric acid. Even special steel tanks would not withstand this chemical action; accordingly, rubber-coated normal steel tanks are used.

2.5 The fibre is washed in an acid or alkaline medium and then desulphurized by means of hot sodium sulphide, soda or caustic soda solution. It is then bleached with NaOCl or H_2O_2 and dried.

These processes also take place in media that cause strong corrosion of the steel, so that rubber-coated normal steel or phenolic resin tanks are used.

2.6 As mentioned under 2.4, the precipitating and spinning bath is renewed on the circulation principle, i.e. it is concentrated at 100° C, the Glauber's salt is precipitated out and the bath is restored to its original concentration with fresh sulphuric acid. The highest corrosion attack occurs in these concentration installations, since acid attack is combined with temperatures up to 100° C and the process is partly carried out in a vacuum.

For all these processes, only rubber-coated normal steel tanks are used.

3. Condition of the factory, problems

A summary of the damage and a series of photographs were prepared by Mr. Draghici. The photographs illustrate the most important instances of corrosion damage. In practice, the condition of the factory is much more serious than is shown by Mr. Draghici's report and photographs. The corrosion, not only of the machines but especially also of the load-bearing reinforced concrete parts, is so far advanced in places that thorough repair work must be carried out immediately. In my view, there are four problem areas, as follows:

3.1 Tanks and pipes

The individual stages of the process were mentioned above. All the tanks and pipes are in a deplorable condition. A general distinction must be made between:

3.1.1 Internal protection and

3.1.2 External protection.

3.1.1 Internal protection

Almost 95 per cent of the tanks in Braila are rubber-coated for corrosion protection. The other parts are treated with fibreglass-reinforced polyester. Rubber-coating is still the optimum protection against the chemical attack in question. Experiments with lining with plastic panels, plastic coatings and whirl sintering have not brought the desired success. For this reason, internal corrosion protection is chiefly provided by rubber-coating in the FRG, as mentioned in connection with the various steps of the process. In contrast to the maximum life of one year in Romania, an average life of 10 years and at least 5 years is expected in the FRG.

In order to achieve optimum rubber coating, several factors are important, namely:

3.1.1.1 The finish and design of the metal structures;

3.1.1.2 The quality of the rubber sheet;

3.1.1.3 The quality of the coating workmanship.

3.1.1.1 Finish and design of the metal structures

VDI guideline 2532 applies in the FRG. In essentials, it contains the following information:

- The profitability of the working processes is partly influenced by the structure;
- Care should always be taken to ensure that the surfaces to be coated can be reached as easily as possible by hand;
- Sharp edges and corners are not permissible. In the case of 90° corners, carefully made fillet welds are generally adequate. The minimum permissible radius is 2 mm. In the case of acute angle corners, sheet inserts must be welded in. The resultant cavities should be drilled from the exterior. Riveting should be avoided.

- Welded joints in the surfaces to be coated must be well made and continuous. The surface must be free of sharp projections, deposits and the like. Inclusions of slag, pores, undercuts and welding beads are not permissible. If necessary, they must be removed by grinding.
- In the case of double-sided welds, overlapping and cavities, the welds must be discontinuous on the side that is not to be coated.
- In order to avoid the formation of bubbles through the inclusion of air arising out of the high temperatures present during vulcanization, the surface of the part must be impervious, smooth and free of pipes and porous spots.
- The prerequisite for a good bond with the steel is that no oil residues (e.g. from machining) or anticorrosive paint (e.g. dipping varnish on standard flanges) are present. Castings may under no circumstances contain washed-in core fragments.
- Tanks that are tested with water pressure must be dried in such a manner that no residual moisture remains in any capillary holes or pores.

3.1.1.2 Quality of the rubber sheet

The sheet used must be absolutely impervious so that no problems arise later. Absolutely impervious covers are made by building up the thickness of the material in several layers at high pressure immediately after calendering. By this method of manufacture, cracks and holes in the surface are completely avoided.

I took away with me some pieces of the unused sheet from Braila; they clearly display air inclusions and are in my opinion not of the optimum quality that is necessary for good work.

3.1.1.3 Quality of the rubber-coating work

The rubber-coating process is carried out in the workshop in Braila. I checked the work on the spot; it is carried out very carefully and in my opinion leaves nothing to be desired.

Essential points of 3.1.1 - Internal anticorrosive protection

I have briefly indicated the factors necessary for satisfactory rubber-coating, as far as I can judge. In that light, one crucial factor is the quality of the rubber sheet, which in my view is not optimal. However, as

I have no practical experience in rubber-coating work, the services of another expert or specialized enterprise should be used. Hoechst AG, Werk Gendorf, Abt. Oberflächenschutz (Surface protection department), D-8261 Gendorf, telephone 08679/75557, telex 056932, is the most experienced enterprise in the FRG.

The Gendorf plant not only produces rubber sheet but also coats tanks with rubber, so that manufacture of the sheet and the coating process are concentrated in one place. For that reason, a technician or expert from the Hoechst works at Gendorf should also be called in to deal with this whole question.

3.1.2 External protection of the tanks and pipes

Most of the tanks and pipes display very marked signs of corrosion. For anticorrosive protection, the tanks are painted on the outside with epoxy resins or perchlorovinyl-base paints.

The protective quality of anticorrosive painting depends on:

The stability of the base material used; and
The quality of the workmanship.

According to my experience, special formulations on a solid epoxy resin base with amine addition compound accelerators, for example, CONCRETIN UA, produced by Messrs. Concrete-Chemie, display outstanding resistance to the sulphuric acid, Glauber's salt and carbon disulphide used as media in the Braila factory. The procedure to be adopted would be as follows:

3.1.2.1 Treatment of the tanks with a steam jet in order to remove all salts from the surface;

3.1.2.2 Sand blasting of the metal surface until bright metal appears;

3.1.2.3 Application of an anticorrosive protection priming on the basis of a solvent-containing epoxy resin system, with zinc phosphate pigments, as required by the regulations of the German Federal Railways, e.g. CONCRETIN ZNP. Consumption of materials, approx. 300 g/m^2.

3.1.2.4 Application of three coats of paint (solvent-containing epoxy resin system with amine addition compound accelerator), e.g. CONCRETIN UA, in an iridescent colour. Consumption of materials, approx. 250 g/m^2 per coat. Interval of one day between application of the successive coats at normal temperature.

Anticorrosive protection of all the pipes and pipe bridges in the open should be carried out in a similar manner to that described above. All of these pipelines display very substantial corrosion and it is absolutely necessary to treat them according to the above-mentioned process.

3.2 Internal concrete structure and floor covering

The buildings in Braila are all of reinforced concrete. Most of them are multistorey structures and the floors are also of reinforced concrete construction. An insulation layer of a butadiene-styrene based product was applied to the raw concrete. A wearing surface of acid-proof clinker in an epoxy mortar was laid on top of that.

All beams, pillars and ceiling undersides were painted with a solvent-containing a perchlorovinyl-based product.

3.2.1 Damage

Signs of sulphate damage can be seen on the reinforced concrete pillars, beams and ceiling undersides. The perchlorovinyl paint used is not resistant enough to the process chemicals and leads to blowing and destruction of the reinforced concrete through reaction of the sodium sulphate with the cement. In places, the concrete has been eroded right through to the reinforcement and the load-bearing reinforcement has been intensively corroded.

The floor covering and the insulation layer underneath it are not impervious, so that sodium sulphate has also been able to penetrate the concrete structure from above and has led to substantial damage.

3.2.2 Repair of the concrete structure

The concrete structure must be carefully examined, particularly to determine its sulphate content. For this purpose, it is necessary to take core samples spaced at certain intervals, to cut the cores into several slices and examine them for their salt content. Furthermore, the strength of the structure must be determined, as it is to be assumed that the high sodium sulphate content has weakened the concrete structure. If the strength no longer corresponds to the values defined by the structural engineer, the concrete must be removed and replaced with fresh concrete either by the sprayed concrete or flow concrete method. Then the fresh concrete must be protected with a suitable epoxy-resin based paint. The individual steps of the process are as follows:

3.2.2.1 Examination of the concrete as described above;

3.2.2.2 Preparation of the base layer by chipping off any loose or crumbling patches and sand-blasting of the exposed reinforcement rods;

3.2.2.3 Repair of the concrete structure on vertical surfaces and overhead by the application of sprayed concrete. In the process, the beams and pillars must be suitably abraded in order to provide an even base layer.

3.2.2.4 Horizontal surfaces such as floors and ceilings should be reconstructed with flow concrete.

3.2.2.5 After intensive preparation of the base layer, minor patches of flaking and damage should be mended and repaired locally with cement mortar to which a dispersion medium has been added.

According to standard plastering practice, these repairs should be carried out by the application of successive layers of maximum 1 cm thickness.

The site of the damage should first be primed with a bonding coat of cement slurry, after which the cement mortar should be applied with a trowel; after the mortar has set slightly, it should be compacted and smoothed with a float.

3.2.2.6 1-3 days after application of the sprayed concrete or cement mortar, the fresh concrete should be primed with a mixture consisting of:

1 part by volume of a solvent-containing non-pigmented, low-viscosity epoxy resin system such as CONCRETIN BT;

1 part by volume of a solvent-containing pigmented epoxy resin system, such as CONCRETIN UA.

Consumption of materials, 300-500 g/m^2, according to the absorbency of the base layer.

3.2.2.7 Two top coats of a solvent-containing pigmented epoxy resin system with amine addition compound accelerator, such as CONCRETIN UA. Consumption of materials, approx. 300 g per coat. Interval between application of the priming and individual coats, one day in each case.

3.2.3 Repair of the floor covering

The floor covering is 95 per cent firmly fixed and is well capable of supporting load; only the joins are not impervious and allow sodium sulphate to pass.

The places that are very badly damaged, where damage is clearly visible on the underside of the concrete structure, must be removed and the concrete structure must be repaired, after which the defective floor covering at those places must be replaced with epoxy mortar. Subsequently, the entire floor must be coated according to the following method with a covering that is resistant to chemicals and can withstand pressure:

3.2.3.1 The floor covering should be examined to detect cavities and poor adhesion of clinker, and any clinker that does not adhere properly should be removed.

3.2.3.2 The entire floor should be intensively cleaned with a steam jet in order to remove all salt residue. The floor must then dry off properly.

3.2.3.3 All faults in the floor covering should be filled in with an epoxy mortar on the basis of a low-viscosity injection moulding resin system, such as CONCRETIN IHS, and levelled.

Composition of the mortar:

3.2.3.3.1 Thickness of layer 0.5 - 1.5 cm
Mixing proportion - 1:9

	Part by weight	Part by volume
CONCRETIN resin for injection moulding	1.0 kg	1.0 l
Special filler (Ballotini)	1.5 kg	1.2 l
Fire-dried glass sand, grain size 0.1 - 0.5 mm diam.	2.5 kg	1.75 l
Fire-dried glass sand, grain size 1.0 - 1.8 mm diam.	5.0 kg	3.5 l

3.2.3.3.2 Thickness of layer 1.5 - 4 cm
Mixing proportion - 1:14

	Part by weight	Part by volume
CONCRETIN resin for injection moulding	1.0 kg	1.0 l
Special filler (Ballotini)	1.5 kg	1.2 l
Fire-dried glass sand, grain size 0.1 - 0.5 mm diam.	2.5 kg	1.75 l
Fire-dried glass sand, grain size 1.0 - 1.8 mm diam.	5.0 kg	3.5 l
Fire-dried glass sand, grain size 3.5 - 7.0 mm diam.	5.0 kg	3.5 l

3.2.3.3.3 Thickness of layer 4 - 10 cm
Mixing proportion - 1:19

	Part by weight	Part by volume
CONCRETIN resin for injection moulding	1.0 kg	1.0 l
Special filler (Ballotini)	1.5 kg	1.2 l
Fire-dried glass sand, grain size 0.1 - 0.5 mm diam.	2.5 kg	1.75 l
Fire-dried glass sand, grain size 1.0 - 1.8 mm diam.	5.0 kg	3.5 l
Fire-dried glass sand, grain size 3.5 - 7.0 mm diam.	5.0 kg	3.5 l
Dry coarse-grain aggregate	5.0 kg	4.2 l

3.2.3.4 Priming of the entire surface with a solvent-free, low-viscosity capillary-active injection moulding resin system such as CONCRETIN IHS in order to close and seal all holes, blowholes, faults and cracks in the floor covering.

Consumption of materials - 400-700 g/m^2 according to the absorbency of the base.

3.2.3.5 Dusting the fresh priming coat with fire-dried glass sand of grain size 0.5 - 1 mm diameter. Consumption of sand - approx. 1 kg/m^2.

3.2.3.6 A special mortar on the basis of a solvent-free, pigmented epoxy resin system with formulated amine accelerator, such as CONCRETIN UBS, mixed in the proportion 1:1 with glass sand of grain size 0.2 - 0.7 mm diameter is applied with a squeegee in a 3 mm layer and is immediately dusted with fire-dried glass sand of grain size 0.5 - 1.5 mm diameter.

Consumption of CONCRETIN UBS binder - approx. 3 kg/m^2;
Consumption of dusting sand - approx 5 kg/m^2.

3.2.3.7 The surplus sand should be swept up next day and the top sealing compound CONCRETIN UBS should be applied.
Consumption of materials - approx. 1 kg CONCRETIN UBS/m^2.

3.3 Outdoor concrete structure

All outdoor exposed concrete structural parts display substantial corrosion damage. In some case the structural parts have not been constructed according to proper concrete practice; in other words, either the concrete mixture was too coarse in grain or the compacting was not done properly or else the freshly made concrete parts were not given any after-treatment. The result is that the surface is relatively porous and is not sealed. The reaction of the lime in the cement with the carbon dioxide in the air has led to carbonation. As a result, the alkilinity of the concrete is lost and corrosion of the reinforcement rods develops. On conversion of the steel into rust, strong expansive forces develop, which lead to peeling of the concrete surrounding the reinforcements. The external reinforcements, which are now exposed, rust very quickly in the very aggressive environmental conditions present in Braila, so that the existence of the structure or structures is endangered. Similar remarks apply to the chimneys and natural draught cooling towers.

In all cases an intensive examination of the concrete is urgently needed, followed by repairs.

The concrete structures should be examined and the repairs carried out according to the method described in the code of practice of the German Concrete Association (Betonverein): "Code of practice 'Repair of concrete structural parts'", which is enclosed. The processes and products and the properties that these products should have are described in detail in the Code. According to Concrete-Chemie practice, the repair work would be carried out as follows:

3.3.1 Examination of the concrete

Extraction of drill cores from the concrete in order to permit determination of the depth of carbonation, the salts content and the strength.

3.3.2

Chiselling out of the defective and adjacent concrete patches, so that the reinforcement rods are exposed as far as the unrusted points.

3.3.3

Derusting of the exposed reinforcement rods and preparation of the concrete underlayer by treatment of the site of the damage with a needle gun or by sand blasting.

3.3.4

Application of anticorrosive protection for the reinforcements in the form of two coats of CONCRETIN ZNP, a solvent-containing two-component epoxy resin system with zinc phosphate pigments, or CONCRETIN IHS-PK, a solvent-free two-component epoxy resin system, with an interval of approx. 5 hours between coats. After the second stage of the process, the site should be dusted with fire-dried glass sand of 0.2 - 0.7 mm diameter grain size.

3.3.5

Application of the bonding coat with CONCRETIN IHS-PK on the treated reinforcements and the concrete at the site of the damage.

Consumption of materials, approx. 500 g/m^2.

3.3.6

Application of cement mortar containing an added dispersion medium, such as CONCRETIN-HS, to the fresh bonding coat. Then proceed as follows, according to the depth of the damage:

3.3.6.1 Up to 5 mm:

With shallower damage, fine-grade CONCRETIN-HS is generally used.

3.3.6.2 5 - 40 mm:

In the case of depths up to 20 mm, coarse-grade CONCRETIN-HS is applied in one coat. For depths over 20 mm it is recommended to apply coarse-grade CONCRETIN-HS in two coats; care should be taken to ensure that the first coat has set and that the mortar is not applied beyond the edge of the damaged area. If necessary, after the coarse-grade CONCRETIN-HS has hardened, fine-grade CONCRETIN-HS is applied with a spatula and the surface is treated with a felt disc or similar tool. Consumption of materials - from 1.7 kg of mortar/mm depth of layer per m^2.

3.3.6.3 In the case of large areas, with a depth of layer of approx. 20 mm, cement is injected after the Torcret system.

3.3.7

Two days after application of the CONCRETIN-HS repair mortar or of the sprayed concrete, an acrylic resin system on the basis of a solvent-containing methyl methacrylate such as CONCRETIN FSS should be applied according to the following method:

3.3.7.1 Priming with colourless CONCRETIN FSS.
Consumption of materials, 200-300 g/m^2, according to absorbency.

3.3.7.2 Application of two top coats of CONCRETIN FSS coloured; consumption of materials, 250-300 g/m^2 per coat. Interval between coats, one day.

Treatment with a solvent-containing acrylate system such as CONCRETIN FSS has the effect not only of after-treatment of the freshly applied repair mortar, preventing the evaporation of the water, but also of providing long-term protection of the entire concrete structure, the following results being achieved in essentials:

- Consolidation of the base layer;
- Protection against thawing agents;
- Steam diffusion capability;
- Excellent protection against carbonation;
- High resistance to weather conditions and aging;
- High light-fastness and chalk-resistance.

Treatment with the acrylate system is absolutely to be recommended in sophisticated technical structures such as chimneys and natural draught cooling towers.

4. Further action

The problems have been exactly described in the last section, but I do not feel competent enough in the area of rubber coating to complete the assignment 100 per cent. For that purpose, a competent staff member of Hoechst AG, Werk Gendorf, should also be called in.

All other problems can be dealt with in direct co-operation [illegible] company. For that purpose, the first requirement would be that th[illegible] substances that have the appropriate resistance properties should be produced or made available in Romania. In the initial phase, the appropriate products could be imported and could later be produced by Cupsik to my formula as a second step.

As soon as the question of substances and materials has been cleared up, the examination of the concrete can begin. For that purpose it is not necessary for me to be present on the site the whole time; the work could very well be carried out by appropriate specialists from my company.

The third phase would consist of the repair work; a specialist from my company would have to be present in order to initiate the Romanian specialists in this work.

The desired visit of two Romanian specialists to the FRG could be carried out as follows:

1. A visit to Concrete-Chemie for familiarization with all the problems of concrete protection;

2. Visit to Hoechst AG, Werk Gendorf, for familiarization with all problems of rubber coating;
3. Visit to Hoechst AG, Werk Kelheim, near Regensburg, for study of all problems related to the manufacture of artificial silk or staple fibre.

I would organize the visit to Rüsselsheim, but it would be absolutely necessary for an official letter to be sent to Hoechst by UNIDO, Vienna, regarding the visits to Hoechst AG in Gendorf and Kelheim.

(signed) Dr. Reinhold Stenner

Rüsselsheim, 11 February 1985