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MATERIALS RESEARCH LABORATORIES

MARIBYRNONG VICTORIA

REPORT

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PROCEEDINGS OF THE SECOND ORGANIC COATINGS SYMPOSIUM HELD AT MATERIALS RESEARCH LABORATORIES 6 AUGUST, 1975

J.T. Hinde (ed.)

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DEPARTMENT OF DEFENCE

AUSTRALIAN DEFENCE SCIENTIFIC SERVICE

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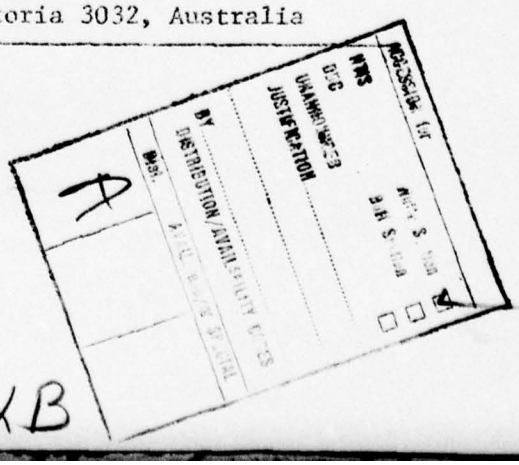

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ABSTRACT

The Proceedings of the Second Organic Coatings Symposium at Materials Research Laboratories provides details of the nine lectures delivered. In addition to recent technical developments in paints the lectures cover such aspects as the formation of phosphate and chromate conversion coatings, assessment of camouflage systems, factors affecting paint deterioration, and the prevention of fungal growth on paints. In addition the problem areas of particular interest to the Services are discussed.

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PROCEEDINGS OF THE SECOND ORGANIC COATINGS SYMPOSIUM

HELD AT MATERIALS RESEARCH LABORATORIES

6 AUGUST, 1975

INTRODUCTION

The Second Organic Coatings Symposium was held at Materials Research Laboratories on 6 August, 1975. A series of lectures was delivered which covered recent technical developments in paints and application techniques and described typical tasks undertaken for the Armed Services. The lectures also indicated the type and extent of practical assistance which the laboratories can offer in the solution of painting and protection problems. An important change in the format from the first Symposium was the inclusion of lectures from representatives of each of the three Services giving the Service viewpoint on painting and painting problems.

The Symposium was opened by the Chief Superintendent, Mr. A.R. Edwards. Chairman of the Symposium was Mr. F. Marson and Mr. L.A. Hill chaired the general discussion at the end of the lectures. Some fifty delegates attended from the Armed Services, Department of Defence establishments and Department of Manufacturing Industry factories. The Conveners of the Symposium were Mr. J.T. Hinde and Mr. P.W. Pettis.

CONVERSION COATINGS AS PRETREATMENTS

L.F.G. Williams

ABSTRACT

Either phosphate or dichromate solutions are used for the pretreatment of metal surfaces prior to painting. The resultant conversion coatings have two major advantages. Firstly, the coating increases the adhesion of the paint to the metal substrate, for example, the use of chromate pretreatments on aluminium. Secondly, it acts as a protective coating by assisting in the prevention of corrosion which would otherwise occur along the metal-paint interface, with a resultant loss of adhesion of the paint film.

The mechanism of formation of phosphate and chromate conversion coatings are reviewed. Some problems which are likely to occur when applying an organic coating over a chromated zinc surface are discussed. Some recent commercial processes developed for the finishing of zinc are also mentioned.

---

1. INTRODUCTION

A conversion coating is formed when a solution oxidizes a metal surface and simultaneously an insoluble film is formed on the surface. The two common types of conversion coatings used as pretreatments for paints are phosphate and chromate conversion coatings. These are applied essentially to improve the adhesion of the organic coating to the metal substrate. However, the conversion coating will also assist in the prevention of corrosion which often occurs along the metal-paint interface with a resultant loss of adhesion of the organic film. Perhaps the most common metal which is susceptible to this type of failure at the metal-organic film interface is zinc and this commonly occurs with galvanized coatings.

2. PHOSPHATING

Phosphating is a well established process used by the Romans in the third century AD (1). The process was developed in the early 1900's by Coslett (2,3) who used firstly ferrous sulphate and later zinc sulphate additives to form phosphate coatings on steel from phosphoric acid solutions. Later, the Parker company used manganous and copper salts to form phosphate coatings (4,5). The advantage of these solutions was a decrease in time of treatment required to form the phosphate coating. By the 1930's, the use of phosphate coatings for the pretreatment of steel surfaces was well recognized and later developments have essentially been in the types of additives used in the phosphating solutions. The literature on these additives has been extensively reviewed by Tinsley (6).

Phosphate coatings on steel fall into one of the categories shown in Table 1.

TABLE 1

THE CLASSIFICATION OF PHOSPHATE COATINGS ON STEEL

	Type	Coating Weight, g/m^2	Fibre Texture
A	Iron Phosphate	0.3 - 0.9	Apparently Amorphous
B	Light Zinc Phosphate	1 - 10	Fine Crystals
C	Heavy Zinc Phosphate	10 - 30	((Coarse Crystals
D	Manganese Phosphate	10 - 40	(

Micrographs obtained by scanning electron microscopy (SEM) in Figure 1 (a to d) show the four types of film formed on steel. Iron and light zinc phosphate coatings are those essentially used for pretreatments for organic finishes although thicker coatings can be used. However, a common use of the thicker coatings is where the surface is required to retain lubricants such as oil which is impregnated in the phosphate coating thereby improving the retention of lubricant. Another important use of these thick phosphate coatings is where cold forming operations require lubricant between the deforming steel and the dye. For this purpose the phosphate coating can be impregnated with surface active compounds such as stearates.

Phosphating solutions contain phosphoric acid and soluble metal phosphates e.g. zinc, calcium and manganese mono- and di-hydrogen phosphates, as well as additives which will be discussed later. The pH of the solution is typically 2 - 3. The crystalline coatings formed on the surface of the metal are a mixture of insoluble phosphates of these metals in the solution as well as salts of the dissolving metal. In the simple case of phosphating of steel in a zinc phosphating solution, zinc phosphate $Zn_3(PO_4)_2$, and ferrous monohydrogen phosphate, $Fe\,HPO_4$, are the predominate species precipitated (7).

2.1 Mechanism of Formation

There are two ways by which insoluble phosphate films nucleate on a metal surface (8).

(a) The first way is by the undesirable process of insoluble crystals suspended in the solution adhering to the surface and this is accentuated on surfaces facing upward in the phosphating solution. The suspended insoluble crystals, often termed sludge, are present in most phosphating solutions after extended use. The correct operation of the bath will reduce this type of nucleation which results in a coating with a coarse grain size and which is undesirable if the coating is to be used as a pretreatment for an organic finish.

(b) The second type of nucleation involves the simultaneous dissolution of the metal and an increase in the pH at the metal surface. The pH of the phosphating solution is balanced to keep the metal phosphates just soluble in the solution. An increase in pH caused by hydrogen evolution at the metal surface will, therefore, precipitate phosphates from the solution. For example, when steel is exposed to a zinc phosphating solution the surface dissolves in the acidic solution according to,

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$$

This depletes the hydrogen ion at the surface and by the mass law effect, the dihydrogen phosphate dissociates according to

$$H_2PO_4^{-} \xrightarrow{-H^{+}} HPO_4^{=} \xrightarrow{-H^{+}} PO_4^{\equiv}$$

The dissolving steel surface produces ferrous ions which are precipitated as the monohydrogen phosphate whilst the zinc in the solution produces insoluble zinc phosphate. This type of nucleation produces fine crystals which are an excellent site for further growth of the film and can be seen in Figure 1 (e and f). The phosphate coating in this case is produced in a zinc-calcium phosphating solution at 65°C with added nitrite. The two SEM micrographs show the nucleation of crystals on the steel. The crystals in Figure 1 (e) were formed in 10S while Figure 1 (f) shows a similar surface after 40S.

2.2 Additives

As indicated earlier, phosphating solutions contain additives which fall into two classes.

(i) Accelerators are added to increase the rate of the hydrogen ion depletion at the metal surface (7). This is often achieved by the use of oxidizing agents such as nitrites, chlorates or peroxides (9,10). Other accelerating agents include copper salts, and organic compounds such as nitrobenzene, aniline, pyridene, and quinioline (7).

(ii) Grain refiners are used to reduce the size of the phosphate crystals formed on the surface (11). This is particularly necessary if accelerators are used and a fine crystal structure is required as a pretreatment for an organic coating. The joint use of accelerators and grain refiners allows films to be formed rapidly at room temperature and they can, therefore, be applied by a spray process (11). Grain refining additives can be alkaline earth phosphates, such as calcium phosphate, as well as other phosphates such as ammonium and triethanolamine (7). Salts of hypophosphoric acid have also been used (12).

2.3 Method of Application

The formation of phosphate coatings on steel is affected by surface grease and films and a cleaning process is usually required. Alkaline cleaning is most common but other methods include vapour degreasing, mechanical cleaning such as grit blasting or emery treatment and solvent cleaning. If

it is necessary to pickle the surface, often a 20% phosphoric acid solution is used. After pickling the surface may require a treatment in a sensitizing solution to promote the formation of a thin fine crystalline coating. This is usually achieved by the use of titanium compounds, such as 0.01% titanium phosphate in a 1% sodium phosphate solution (13,14). Colloidal titanium solutions have also been used.

This sensitor controls the nucleation of the crystalline phosphates from the phosphating solution, and results in a fine grain, highly adherent, highly corrosion resistant coating. These sensitizers are also used when phosphating zinc die castings or galvanizing to avoid the large crystalline coatings which normally form on zinc.

The use of iron phosphating solutions on steel may enable the pretreatments to be avoided. Relatively clean steel surfaces can be successfully phosphated by the addition of surface active agents to the iron phosphating solution (15,16). Basically, iron phosphating is a four stage process as shown in Table 2. The chromate treatment is optional and is used to improve the corrosion resistance of the film. A dilute solution of 0.02 to 0.1% CrO_3 is used and results in the incorporation of chromate in the phosphate coating (17,18). This chromate gives added corrosion resistance as it is a corrosive inhibitor for metals like iron, zinc and cadmium.

Zinc phosphating produces a thicker film with a greater corrosive resistance than that produced by iron phosphating solutions (7). A typical process for zinc phosphating steel is also outlined in Table 2.

TABLE 2

TYPICAL PHOSPHATING PROCESSES

FOR THE PRETREATMENT OF STEEL

Iron Phosphating	Zinc Phosphating
(a) Clean and phosphate in one process	(a) Clean
(b) Rinse	(b) Rinse
(c) *Chromate treatment	(c) *Activate with Ti Compounds
(d) Dry	(d) Zinc Phosphate
	(e) Rinse
	(f) *Chromate Treatment
	(g) Dry

* These steps are optional

Phosphating is used as a pretreatment for iron, zinc and cadmium surfaces. Aluminium is usually coated with a chromate conversion film as a pretreatment.

3. CHROMATE CONVERSION COATINGS

Chromate conversion coatings are most commonly used on aluminium as a pretreatment for organic coating. A chromate coating on aluminium will not only increase the adhesion of the paint, but will offer the metal added corrosion resistance. This is evidenced by the fact that some specifications for the surface finishing of aluminium (i.e. without any final organic coating) offer anodizing or a chromate conversion coating as alternatives. Under conditions where the surface is not exposed to any abrasion, the corrosion resistance of anodized and chromated surfaces are comparable. There can be a problem with high copper containing alloys (19) which are not well protected against marine environments by the use of these chromate conversion coatings.

Chromate conversion coatings can be applied to aluminium, zinc, cadmium, brasses, copper, magnesium, silver and other metals (20,21). Chromating is a relatively new process which was developed as a protective coating for zinc during World War II (22). The process stopped the formation of white corrosion products which otherwise formed on zinc under high humidity conditions.

The chromating reaction occurs in acidic dichromate solutions (20) and results in the formation of Cr(III) which precipitates as the hydroxide at the metal surface. This occurs because the oxidation-reduction reaction at the metal surface results in a depletion of hydrogen ion, thereby allowing the chromic hydroxide to precipitate, i.e.,

$$Cr_2O_7^{=} + 8H^{+} + 3\ Zn \rightarrow 2Cr(OH)_3 + 3Zn^{2+} + H_2O$$

Some of the unreacted chromate is adsorbed in the film and this improves its corrosion resistance. Although the reaction appears to be simple, this is not the case.

In pure chromic acid solutions, a chromate conversion coating is not formed as anion additives are required to activate the reaction. Typical additives for solutions for the chromating of zinc contain sulphate or chloride. Thin colourless films on zinc are formed if fluoride is added to the solution. Thin films on brass are formed with sulphate additives whilst the thicker films require the presence of chloride ions (23). Chromating solutions for aluminium contain fluoride as well as phosphate which produce a film containing amorphous chromic hydroxide and crystalline phosphates (24).

The heating of thick chromate conversion coatings on zinc will result in dehydration of the film and a cracking of the coating (20). This phenomenon can present a problem if a stoved organic coating is used over the chromate coating. If the chromate coating is air dried in the normal manner, the film would contain some water. After painting, the composite coating, when stoved, would result in release of water from the chromate film and a loss of adhesion of the organic coating. Therefore, it is suggested that the chromate coating should be pre-heated if a stoved organic coating is to be used. Heating at 60°C for two hours should be sufficient for this purpose.

This temperature will dehydrate the chromate coating without a drastic change in corrosion resistance which can occur at higher temperatures (25).

4. RECENT DEVELOPMENTS

Two recently developed processes are being marketed in Australia which are essentially for the finishing of zinc diecastings.

The first is a chromate coating applied from an alkaline bath by the use of a constant a.c. current of 40 mA/cm^2 (26). During the process, the potential is monitored and the current is interrupted at a predetermined potential. If the potential reaches 200 V, a 30-37 µm coating is formed with an increase in size of the component of 25 µm per side. The coating consists of metal oxides and has excellent corrosion resistance. The coating is more abrasion resistant than normal chemical conversion coatings, but the components are not easily soldered and the coating has a high electrical resistance. X-ray diffraction revealed two phases, NH_4ZnPO_4 and $ZnCr_2O_4$ (27).

The other development is called the Zincart Process. This involves the formation of a chromate conversion film from a chromic acid solution containing chloride. The chromate conversion coating is then coloured by the adsorption of a dye. Once coloured the components are finished with a clear organic coating. The advantages of this process is that an attractive iridescent coating is formed in a range of colours and the coating is highly corrosion resistant.

QUESTIONS

B. Wearne, G.I.N.D. Navy

Q. How long should soft chromate coatings age before being painted?

A. We believe that at least 24 hours should elapse before painting; alternatively the chromate coatings may be lightly stoved before painting.

N. Seabrook, M.F.P.

Q. Could you advise on the derusting and re-phosphating of recovered articles.

A. After derusting and cleaning, a commercial sensitiser should be used before phosphating.

COMMENT

R. O'Donnell, W.P.E.

We recommend the use of a hydrochloric/sulphuric acid bath treatment before re-phosphating. We consider chromate treatment after iron phosphating is unnecessary. We use an etch primer on non-ferrous metals.

F. Brennan, D.A.O.A. Army

Q. Is phosphating mainly to provide a key for paint or to stop corrosion?

A. Phosphating improves the adhesion of subsequently applied paint and reduces corrosion undercutting of paint films.

B. Mcarne, G.I.N.D. Navy

Q. Are there any problems with the new treatments?

A. The treatments are in the early stages so the problem areas are not completely defined.

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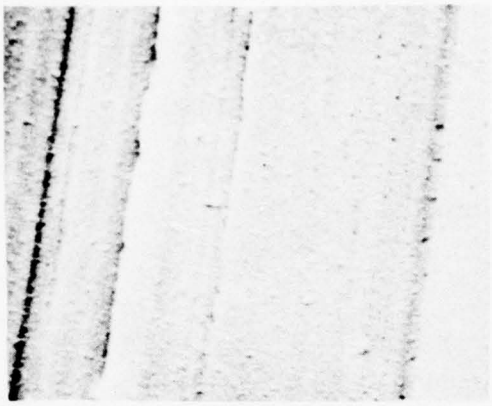

(a) x 3,800

(b) x 360

(c) x 360

(d) x 360

(e) x 4500

(f) x 170

Figure 1 shows SEM photographs of phosphate coatings on steel:

(a) an iron phosphate

(b) a light zinc phosphate

(c) a heavy zinc phosphate

(d) a manganese phosphate

(e) & (f) the initiation of crystals on the steel surface after immersion in a typical zinc phosphating solution for 10 and 40S respectively.

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ACCELERATED WEATHERING

C.A. Grey

ABSTRACT

Details are given of the instruments used in the accelerated weathering of paints in the laboratory. Trials carried out to determine the most effective method of use of these instruments are discussed. Included are several basic trials which provided information firstly on the reproducibility of the results obtained from different instruments of the same type. Secondly the results of accelerated weathering in instruments of different types are compared with those obtained on outdoor weathering. In addition several trials aimed at determining actual changes in paint films during accelerated weathering are also discussed.

It is concluded that the most reliable use of accelerated weathering equipment at the present time is for the comparison of materials of similar type.

---

1. INTRODUCTION

The evaluation of paint or related materials generally requires some knowledge of their durability or weathering properties. However, it is often not practical to wait the lengthy period, sometimes 5 to 10 years, required to obtain reliable weathering information. To decrease the time involved, paints can be exposed in an instrument designed to simulate and accelerate the weathering process.

2. TYPES OF INSTRUMENTS

The instruments consist of a light source, to simulate sunshine, water sprays to simulate rain and air treatment equipment for controlling temperature, relative humidity and also environmental contaminants. Test panels are usually placed on a rack which rotates around the light source and water sprays so that all panels receive a uniform exposure.

A number of light sources can be used in the instruments. Early attempts to simulate sunlight used mercury arc lamps. This was followed by the enclosed carbon arc lamp. The radiation from both of these lamps differed significantly from sunlight in the ultraviolet region and therefore exposure of paints to these lamps gave different results to outdoor weathering. The enclosed carbon arc lamp, which operates in a partial vacuum, was found to accelerate color changes and chalking of paints but had little effect on actual film properties. However, this made it useful for the evaluation of the

decorative properties of paints and the use of this light source is still a requirement of many specifications. The development of the light sources continued through the open or "sunshine" carbon arc, the xenon arc lamp and special fluorescent lamps. These three types of lamps resemble sunlight more closely and are now the preferred light sources for accelerated weathering equipment.

Rain is simulated in artificial weathering instruments by a gentle water spray and since rain is virtually a form of distilled water some means of purifying the water used in the instruments is necessary. A common method for this purification is the use of twin bed demineralizing resins. Failure to carry out this precaution can result in considerable discoloration of the paints due to staining from the iron and other salts in tap water.

The operating temperature in the accelerated weathering unit should also be under reasonable control. Excessively high temperature may bake some paint films and make them more durable while too low a temperature may retard the weathering process. Usually the instruments are operated at an air temperature of approximately 40°C to 45°C.

The instruments can generally be programmed to control relative humidity. It has been found that higher humidities promote chalking of paint films. Some instruments can be operated with periods of high and low humidity and this results in a severe test for evaluation of the chalk resistance properties of paint films.

Exposure of the test pieces to contaminated atmospheres is an additional procedure sometimes used in an accelerated weathering test. Such tests include exposure to atmospheres enriched in oxygen, ozone, sulphur dioxide or oxides of nitrogen.

3. EXPERIMENTAL TRIALS

A number of trials involving accelerated weathering have been undertaken by Paints Group at MRL to determine how the instruments can best be used to solve consulting problems. The following sections summarize the results obtained in several of these trials.

3.1 Reproducibility of Accelerated Weathering Tests

A co-operative test trial to examine the reproducibility of results obtained from different artificial weathering units of the same type has been carried out. Three "Atlas Weatherometers" were used and all were operated according to the requirements of AS 1580 Method 483.1 Type D which is equivalent to the twin carbon arc method of ASTM G23 Type D, Using this method there is automatic control of temperature and water spray cycle but no control of humidity. The method is the one most often quoted in Australian paints specification.

Six paint systems were exposed in the instruments for 1000 hours. They were assessed after each 100 hours during this period.

There was little difference between the discoloration of the paints in the three instruments although a slight brown stain developed on the finishes in one instrument. This almost certainly resulted from unsatisfactory treatment of the water entering the instrument. However, the rate of loss of gloss and chalking of the paints varied slightly between the instruments.

In addition to the paint samples light sensitive plastic chips conforming to ASTM D1920 were also exposed. The transmission of these at 410 nm were measured every fifty hours during a total exposure period of 200 hours. A log-log graph of the transmission of the chips against the exposure time produced straight line graphs the slope of which represented the light dosage from the lamps. The actual graphs produced from the trial varied significantly in slope and indicated that there was a difference in the lamps in different instruments.

In general the trial showed that if comparison of results from different artificial weathering units of the same type are to be made then the instruments should be used with maximum control of operating conditions. For example arc lamp voltage and current, temperature, water condition, etc., should be maintained at a predetermined value. Also it would probably be preferable to operate the instruments at a constant humidity. This would mean that the Atlas instruments used for the trial would need to conform to the Type DH instruments of the appropriate Australian or ASTM specification.

3.2 Comparison of Different Enclosed Carbon Arc Artificial Weathering Instruments

The behaviour of several paint systems in different types of enclosed carbon arc lamp artificial weathering instruments has been investigated. The instruments used in the trial were :

(a) An Atlas Weatherometer operating to the conditions specified in the American ASTM G23 for type D instruments.

(b) A Marr Artificial Weathering Unit operating to the conditions specified in the British test, DEF 1053 Method 26.

(c) An Atlas Fadeometer operating to the conditions specified in the American ASTM G25 Method B. That is with the inclusion of a humid dark period.

A series of alkyd enamel type paints were exposed in these instruments and were also subjected to 45° natural weathering.

Some correlation existed between the rate of discoloration of the paints in the test instruments and on exterior exposure although the acceleration rate in each instrument was different.

The rate of loss of gloss on natural exposure appeared to be more dependant on the season of the year and periods of slow and fast degradation for this property were observed. No direct relationship for loss of gloss under natural and artificial exposure could therefore be derived.

The instruments varied considerably in their rate of chalk production. No chalk formed on the paint in the "Fadeometer" and it appeared that the humidity level was too low to produce this effect. None of the instruments showed any correlation with the deterioration occurring on natural weathering which again appeared to be dependant on the season of the year, the washing off of chalk, etc.

The trial generally confirmed that none of the instruments correlated with outdoor weathering. In addition the different types of degradation

occurred at different rates relative to one another in the test instruments and outside. It would therefore appear that it is not possible to evaluate a series of paints for all defects in artificial weathering instruments.

3.3 Comparison of Paints of Similar Type

Because of the results of the above trials and those of other workers it is believed that the main use of artificial weathering units at this stage is to compare paints of similar composition. A number of trials such as this have been carried out and the following sections discuss a selection of our results.

3.3.1 Olive Drab Alkyd Enamels

One example of such a test was carried out on Olive Drab Enamels. These were all based on alkyd resins with chromic oxide as the main pigment. Two series of paints were involved, one being full gloss and the other lustreless. The paints were examined in a twin enclosed carbon arc "Atlas Weatherometer". They were also exposed to natural weathering at temperate semi-industrial and tropical-rural test sites. At the completion of the tests the paints were arranged in order of merit. The order for the lustreless materials is given in Table 1. Because the paints are commercial products they have been designated by a letter. Spearman Rank correlation coefficients for the outdoor exposures at temperate and tropical sites compared to the artificial exposure were 0.98 and 0.97 respectively. These high correlation coefficients indicate that the artificial test is suitable for screening the poor paints from the good ones. Similar results were obtained for the gloss enamels.

TABLE 1

ORDER OF MERIT OF LUSTRELESS OLIVE DRAB PAINTS

Paint	Position After: Natural Weathering		Accelerated Weathering
	Temperate	Tropical	
A	24	24	24
B	21	20	19
C	14	13	14
D	22	22	22
E	12	15	12
F	2	4	1
G	13	10	11
H	23	23	23
I	3	2	2
J	1	1	3
K	8	6	9
L	9	12	10
M	6	5	5
N	19	21	20
O	15	12	15
P	17	16	16
Q	7	8	6
R	16	19	18
S	20	17	21
T	11	11	13
U	18	18	17
V	10	9	8
W	5	7	7
X	4	3	4

3.3.2 Epoxy-Polyamide Paints

A second trial carried out consisted of a series of epoxy-polyamide paints, all pigmented white. These paints were exposed to artificial testing in a twin carbon arc "Atlas Weatherometer" and to natural conditions at a temperate semi-industrial test site.

The main failure that occurred was chalking and this was assessed according to the Australian Standard using a scale of 10 indicating no chalk and 0 severe failure. The results are shown in Table 2.

TABLE 2

CHALKING OF EPOXY-POLYAMIDE PAINTS

Paint	Natural Weathering (18 months)	Artificial Exposure (1000 hrs)
A	6	6
B	5	4
C	5	6
D	5	4
E	4	4
F	6	6
G	4	4
H	6	7
I	7	8

The results from these two exposures appear to be fairly similar and in fact a brief statistical analysis using a "t" test showed that there was no significant difference between them. We did find that many of the epoxy materials tended to yellow slightly more in the artificial weathering instruments than they did outdoors. However, it was concluded after a larger series of tests that "Weatherometer" exposure was a suitable screening test for the epoxy-polyamide materials of similar pigmentation.

3.3.3 Additional Trials

The preceding two examples illustrate how the artificial weathering test can be used as a screening method for materials of similar type. It appears that this is the most reliable use for these instruments.

Using both carbon and xenon arc lamp instruments we have successfully screened a number of series of similar paints. Examples of the additional trials carried out are :

A. Acrylic latex emulsion paints in a number of colors.

B. Grey and White aliphatic polyurethanes.

C. Grey and White air drying acrylic lacquers.

D. Black stoving epoxy paints.

E. Grey vinyl paints.

3.4 Chemical Changes Occurring in Paints Exposed in Artificial Weathering Instruments

Because of the inconsistencies arising between artificial and natural weathering some fundamental work has been carried out to determine the changes occurring in coatings during exposure to both of these conditions.

One method of approach has been to use attenuated total reflectance techniques to obtain the infrared spectra of paints after various periods of exposure. The results obtained help to indicate some of the chemical changes occurring in the artificial weathering instruments. An example of this is the oxidation of a soya alkyd resin. This material was exposed in carbon and xenon arc lamp artificial weathering instruments and to natural weathering. The ATR infrared spectrum was measured after various periods of exposure and changes in the carbonyl peak relative to the carbon-hydrogen peak were measured. A number of differences were observed in this analysis. The main difference being the more pronounced oxidation in the carbon arc lamp instrument while the xenon arc and the natural exposure were approximately the same. However, the mechanism of degradation of alkyds is extremely complex and therefore the results at this stage can only be used as a method for comparison of instruments.

A more complete study is being undertaken because of the results obtained. In this study different groups are being analysed in a series of alkyd and acrylic resins by both the ATR infrared technique and also using an ultraviolet reflectance technique.

3.5 Variation in Physical Properties on Artificial Weathering

As well as studying the chemical changes which occur on artificial weathering some work has been done on changes in physical properties.

3.5.1 Adhesion Changes

It has been reported that the adhesion of paint films vary with the season of exposure but the general trend is to increase slightly soon after exposure and then decrease on prolonged weathering.

Several types of paint films have been exposed to xenon arc artificial weathering and the adhesion measured after various times of testing using a torsion method.

The results from this exercise indicated that the adhesion of most paint films increased for an appreciable time of exposure. Typical adhesion changes found are :

(a) An alkyd which increased from 201 Kp cm^{-2} to 286 Kp cm^{-2} in 1600 hours.

(b) A polyurethane which increased from 296 Kp cm^{-2} to 347 Kp cm^{-2} in 1600 hours.

(c) An epoxy which increased from 287 Kp cm^{-2} to beyond the range of the test instrument of 400 Kp cm^{-2}.

These results indicate that in the accelerated weathering instruments no degradation of this property has occurred and that probably no stresses, which are partly the reason for adhesion failure, have been "set-up" in the paint film.

3.5.2 Changes in Tensile Strengths of the Film

A number of clear varnishes have been exposed in a twin carbon arc instrument and after various times of exposure, tensile properties measured on them using a Cambridge Extensiometer. The results of the experiment are shown in Table 3. This shows that a tung oil varnish had a comparatively high Young's Modulus and a low extension at break which means that it is a fairly hard and brittle varnish. After exposure in the artificial weathering instrument it became too brittle to enable measurements to be taken. The epoxy ester and alkyd varnishes were initially soft and tough as indicated by the low Young's Modulus and the large extension at break. After weathering the epoxy ester varnish became hard and brittle. This is shown by the much higher modulus and much lower extension at break. The alkyd varnish after weathering became only a little harder and gradually lost its ability to stretch.

The varnishes were also exposed to natural weathering on wood and their performance in general was that indicated by the tensile measurements after artificial weathering. The order of performance was alkyd best followed by epoxy ester and tung-oil phenolic.

TABLE 3

MECHANICAL PROPERTIES OF VARNISHES

Varnish	Exposure Time (hours)	Apparent Young's Modulus (k Pa)	Load (k Pa) at extension of		Ext. at Break %
			2%	5%	
Tung oil phenolic	0	68.9×10^4	13.5×10^3	b	3
	80	too brittle to handle			
Trimethanol propane epoxy linseed ester	0	6.2×10^4	0.7×10^3	1.1×10^3	124
	80	121.6×10^4	9.0×10^3	b	2
	200	too brittle to handle			
Isophthalic alkyd	0	2.8×10^4	0.007×10^3	0.3×10^3	100
	80	3.4×10^4	0.2×10^3	0.4×10^3	91
	200	13.6×10^4	2.5×10^3	3.2×10^3	76

b = Film broke

4. CONCLUSIONS

The conclusions which can be drawn from the above results are :

(1) The most reliable use of accelerated weathering at the present time is the comparison of materials of similar type. For example if a particular type of paint is to be used, then accelerated weathering can screen the effect of variation in formulations much more quickly than natural weathering.

(2) Accelerated weathering can also be used as a preageing technique before some other particular property is examined. That is, accelerated weathering can be used to study the effect of weathering on properties such as flexibility, hardness, abrasion resistance, resistance to fuels, solvents and lubricants or attack by mould or algae. However we have not successfully been able to use accelerated weathering to follow changes in properties which depend on internal stresses being developed in the film, for example, adhesion and cracking failures.

QUESTIONS

L.A. Hill, M.R.L.

Q. Which varnishes performed best on weathering?

A. Polyurethanes, although quality is variable; alkyds and spar varnishes were also good.

W/O C.V. Hart, HOSC RAAF

Q. Are there any standard test methods for accelerated weathering?

A. Yes, AS 1580 and ASTM methods.

R. O'Donnell, WRE

Q. What is the effect of temperature on accelerated weathering? How does it relate to practice?

A. The temperature in the machine can be controlled. If it is too high the paint films bake and the results are erroneous. It is difficult to relate accelerated weathering conditions to natural weather because there is no standard climate. Florida is often used as a "Standard" climate.

W. Hall, M.R.L.

Q. How does exposure in Innisfail compare with exposure in Melbourne?

A. The order of merit is usually the same but Innisfail is more severe e.g. a chalk rating of 7 in Melbourne corresponds to a rating of 5 in Innisfail for the same period of time.

LABORATORY SIMULATION OF CAMOUFLAGE

D.P. Skinner

ABSTRACT

The design of paint schemes for military vehicles may involve the minimising or maximising of visibility under specified conditions. Visibility cannot usually be calculated for real situations, and field trials may prove impracticable, particularly for new vehicles yet to be delivered. A simulation technique is therefore necessary.

The system to be described is a modification of the cinematographic technique of front projection, in which a reflex screen is used to provide a background derived from a normal colour transparency. Methods have been developed to allow a model vehicle to appear to be imbedded within a real scene, and to modify, within limits, the apparent colour of the model. Photographs produced in this way are suitable for measurement on a visibility meter.

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1. INTRODUCTION

One of the factors affecting the choice of paint schemes for vehicles, particularly in Defence organizations, is consideration of the visibility of the vehicle in its expected environment. It may be necessary to maximise visibility for safety purposes, as with training aircraft for example, or to minimise visibility, usually for the camouflage of armoured fighting vehicles. Calculation of the visibility of a vehicle in a complex background is beyond the scope of present theory, and therefore experimental methods must be used. Frequently, for reasons of cost or availability, the experimenter will not have access to the vehicle.

Simulation of the presence of a vehicle is no problem, since many excellent kits are commercially available for the construction of 1/35 and 1/72 scale models. Simulation of an environment for the vehicle is quite another matter. One might suppose that a model vehicle belongs naturally in a model terrain, but the construction of a number of different examples of each of several types of terrain is not a very practical proposition, and it is doubtful if realistic models could be made to simulate, for example, tropical rain-forest. The use of a single model terrain has, however, been successfully applied (1) to the problem of the recognition of vehicles under nets in lightly wooded grassland.

Where a model terrain is impracticable, it becomes necessary to use a real terrain either "live" or in photographs. In practice the use of photographs is much the more attractive alternative since it reduces the investigation from a field exercise to a laboratory experiment. Colour photographs in the form of paper prints one or more square metres in area are feasible, but less than ideal in colour rendering. Colour transparencies of similar size also have practical disadvantages (including cost). The choice of techniques is therefore reduced to the combination of 1/35 or 1/72 scale models with standard sized (36 x 24 mm or 60 x 60 mm) colour transparencies.

2. EXPERIMENTAL APPROACH

The experimental approach adopted at ERL is a variation of the technique of front projection (2), which does not appear to be widely known, despite its use on cinematography (3-5), television and advertising photography. The principle of the technique is illustrated by Figure 1. A standard slide projector contains the background scene in the form of a 36 x 24 mm colour transparency. Light from the projector passes through a variable optical attenuator (crossed polarisers) and comes to an 8-μm thick uncoated pellicle beam-splitter. Approximately 92% of the light passes through the beam-splitter and is absorbed in a black velvet light-trap; the remainder expands to form a focused image on a screen. This screen is covered with a retro-reflecting material (3M Scotchlite High Gain Projection Screen) of very high gain*, which has been reported (4) as around 1600. Most of the light reaching the screen is reflected back along its path, so the beam converges and the intensity of the light flux increases with distance from the screen until, after passing through the pellicle, the flux density reaches a maximum at a position corresponding to the projector. A camera is placed at this point, as shown in Figure 1. The image on the screen, as seen from this position, is considerably brighter than that from the same projector used at the same distance on a matt white screen, despite the fact that, typically, less than 1% of the available light is used in the present arrangement.

If an object, shown in Figure 1 as a model battle-tank, is placed in front of the screen, any light from the projector that falls on the object is reflected diffusely, so that the intensity of the resulting light flux decreases with distance from the object. The ratio of light fluxes from the screen and from the model is so great at the camera that, in the absence of additional illumination, the model appears black, even if painted white. Naturally, the model throws a shadow on the screen, but this shadow is not visible at the camera position, which is effectively on the same optical axis as the projector. For the same reason, the model may be mounted on a small piece of reflex screen (as shown) without the join between the screens being obvious.

Illumination for the model is provided by a lantern with a movable mirror to simulate the variable position of the sun. The model is thus seen from the camera position by the usual process of diffuse reflection. Any light from the lantern that reaches the retro-reflecting screen is reflected back to the mirror, and is therefore invisible from the camera position.

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* The gain of a retro-reflecting screen is the ratio of light intensity reflected back along the angle of incidence to that from an ideal diffuser under the same conditions.

One way in which the present apparatus differs from a normal cinematographic front-projection system is that the lantern used to illuminate the model is provided with coloured filters, and most of the model is painted white. The white parts of the model can thus be made to appear the colour of the filter used, and, by a suitable balancing of intensities between the projector and the lantern, different apparent luminous reflectances can be achieved. For example, an orange filter could be used to make the vehicle appear orange, but the apparent colour could be changed to a reddish brown simply by reducing the intensity of light from the lantern or by increasing that from the projector.

The remaining part of Figure 1 is a telephotometer that may effectively replace the camera for the measurement of colour or relative luminous reflectance in the composite scene. The telephotometer may be brought into use by the insertion of a mirror as shown.

3. SIMULATION FACTORS

There are a number of practical considerations in obtaining a realistic representation of a vehicle/background combination, and by far the most important of these are shadowing and scale. The model vehicle seems to be hovering in the air unless a suitably shaped shadow appears on the background, and the shadow itself looks like a tarpaulin on the ground unless the background is partially visible through it. The method of simulating such a shadow is to cut a suitable shape from a piece of cardboard and attach it to the road-wheels of the vehicle. The background can be made partially visible through the shadow by double-exposure photography. The problem of scale is somewhat more obvious; the vehicle must appear to be of a suitable size compared with objects that seem to be near it. This is achieved by photographing the background scene from a suitable distance, which is calculated from a simple formula.

There are also a number of factors that one would expect to be important, but in practice seem to be almost irrelevant to the realism of the picture. The most surprising of these is that the direction of the simulated vehicle shadow need not be in the same as that of the background shadows, provided it is consistent with the lighting of the model. The texture of the simulated shadow is also unimportant; a smooth-edged shadow on an obviously rough surface appears quite realistic. Perspective errors may be introduced unless the composite picture is photographed from a suitable distance, but again these are not too disturbing.

The simulation of pattern-painted vehicles presents a further problem, since patterns would be expected to contain at least three colours, and the techniques presented here give only one degree of freedom in colour. One solution would be to paint each pattern in full colour and to illuminate the model in white light, but this would involve re-painting the model for every minor change in colour. The solution adopted was to paint the model in black, white and desaturated magenta (puce). This combination when illuminated with a yellow-green light appears black, olive and grey-brown (for forest camouflage) and when illuminated with a yellow light appears black, fawn and red-brown (for desert camouflage).

4. ASSESSMENT OF EFFECTIVENESS

In order to assess the effectiveness of a camouflage scheme in a composite photograph, it is necessary to make an objective measurement of the visibility of features in the photograph. At MRL, it is intended to do this with a contrast-reducing visibility meter (6) of the very simple design shown in Figure 2. In this, there are two routes by which the eye can see a target, which is one of the composite photographs. One route gives no distortion; the other route gives a completely defocused view. By using polarising filters in the two routes and a rotating polariser in the eyepiece, it is possible to fade smoothly from a clear view to a defocused view by rotating the eyepiece. When this is done, parts of the image disappear at different times, depending on how visible they are. Therefore the angle of the eyepiece when a feature disappears is a measure of the visibility of the feature. The visibility of a standard target in the form of a grey disc can be measured in the same way. It is also possible to make an objective measurement of the contrast of this type of target by measuring light transmission. Thus, a series of targets can be used to calibrate the visibility meter, and so obtain an equivalent contrast for any feature in a picture. For example, it might be possible to say that the upper track on a tank has an equivalent grey contrast of 0.7, whilst the main gun barrel has a contrast of only 0.5. In this hypothetical case, it would be futile trying to camouflage the gun barrel until something had been done about the shadows around the track.

This part of the research has reached the stage where there is evidence that the visibility meter will work. Some calibrations have been carried out using the grey discs, but no serious measurements on photographs have been made. One thing that is not certain is whether different observers will get the same results on the same pictures, even if their calibrations are different.

The anticipated use of the two techniques, front projection and the visibility meter, is as follows. Photographs will be taken to simulate a number of vehicles in different colours against various backgrounds, and the effective contrasts of the more visible features will be measured. Patterns will then be painted on the vehicles in an attempt to suppress the most visible features, and the measurements repeated. It is hoped in this way to converge on a pattern system that is optimum for each vehicle over a wide range of conditions.

5. CONCLUSION

It is emphasised that the final assessment of any camouflage system can only be in the form of a field trial using real vehicles and experienced military observers. The purpose of the experiments described in this paper is to discover the systems of pattern painting that will be most profitable to investigate when vehicles become available for field trials.

QUESTIONS

N. Seabrook, M.E.F.

Q. Is it possible to project a pattern on the model instead of painting the model?

A. We have considered the possibility of doing this, and it could be practicable, but we have not yet tried it out.

L.A. Hill, M.R.L.

Q. Is there any value in camouflage to prevent detection of a moving vehicle?

A. It is very difficult to camouflage a moving tank. Bold disruptive patterns make moving objects more difficult to observe.

W. Hall, M.R.L.

Q. What consideration are you giving to infra red reflectance requirements?

A. We have given this a lot of consideration. However the infra red reflectance of vegetation is hard to mimic. Cobalt titanate pigments are promising but there are still many problems to solve.

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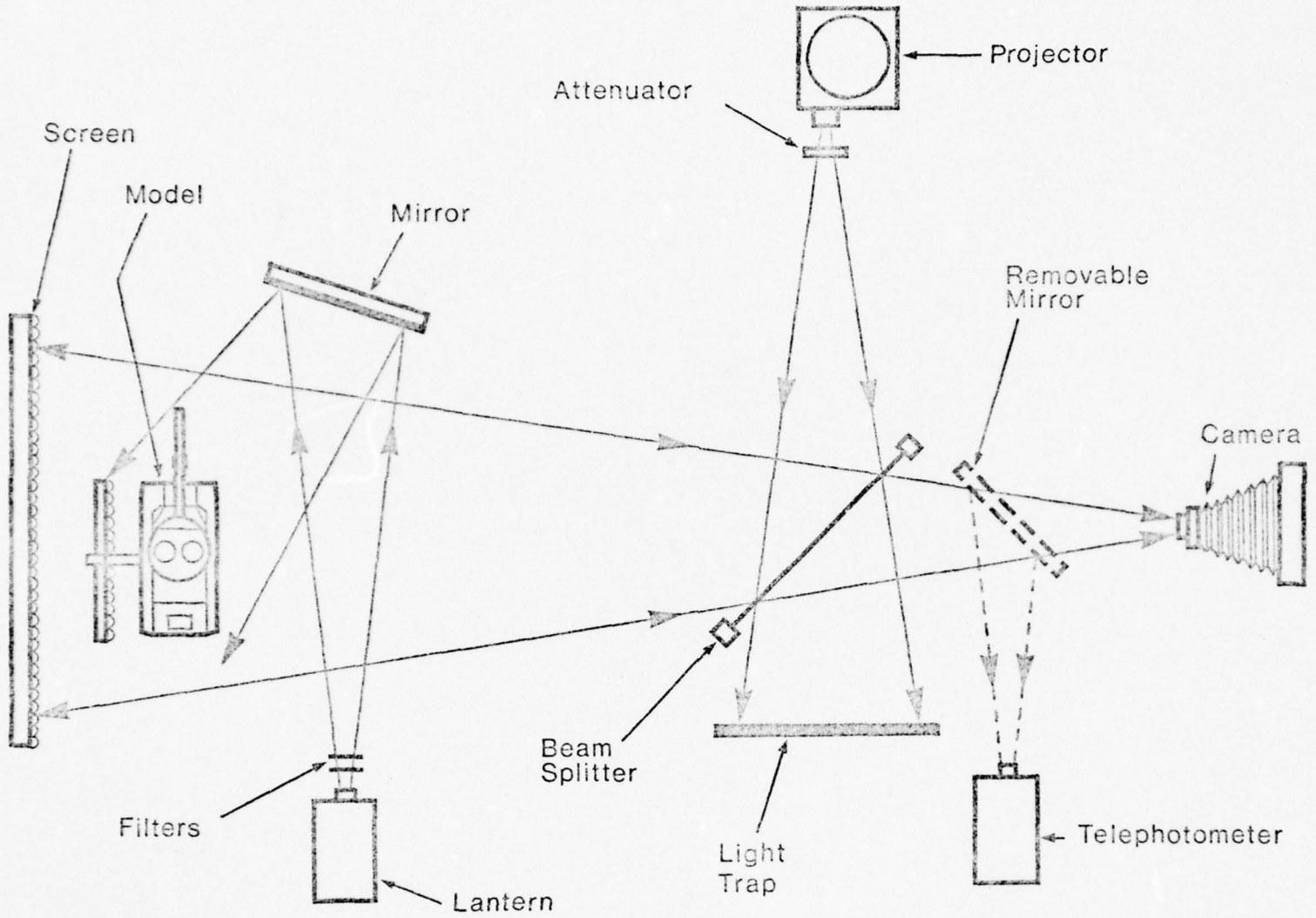

FIG. 1 LAYOUT OF FRONT-PROJECTION SYSTEM

PRECEDING PAGE BLANK-NOT FILMED

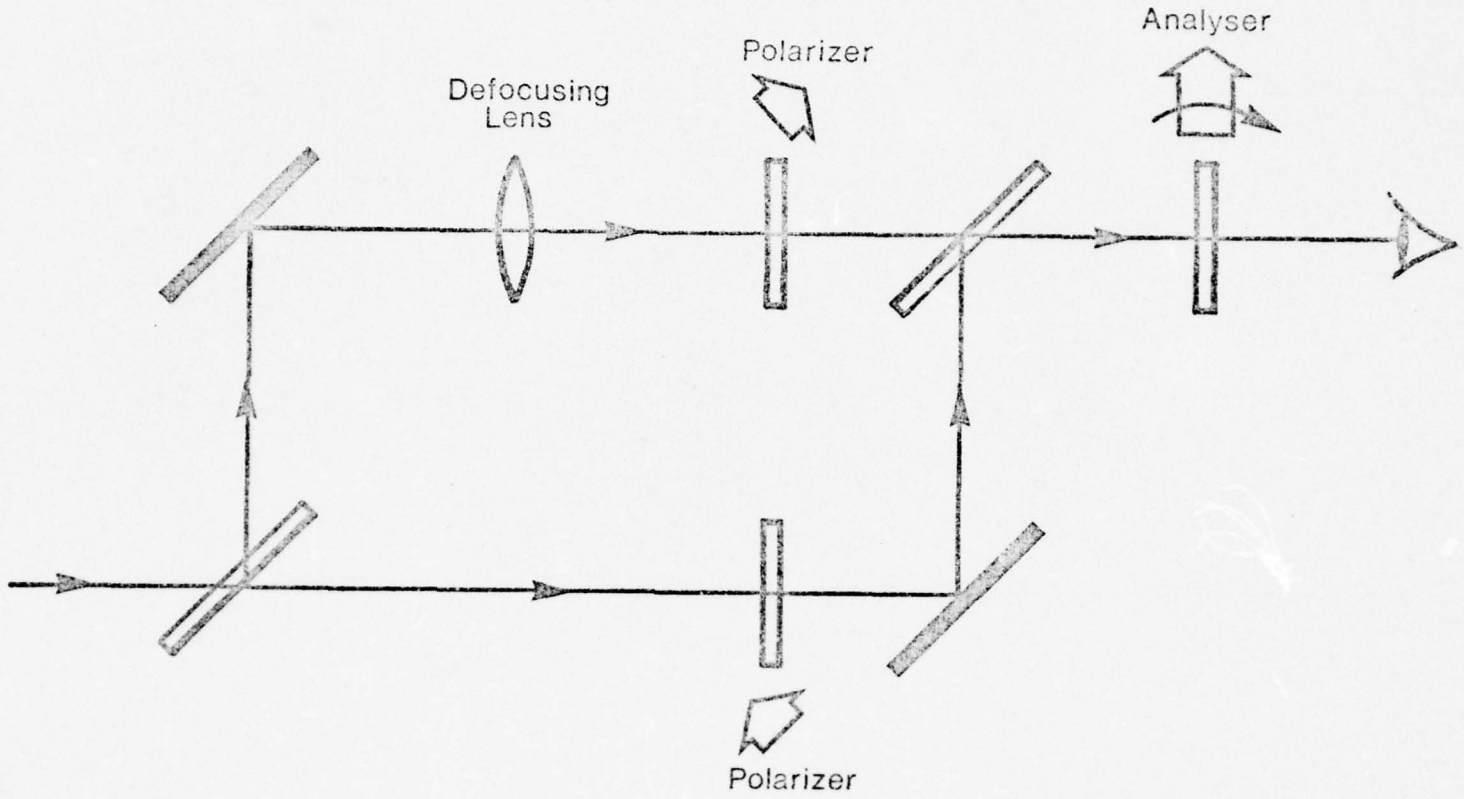

FIG. 2 LAYOUT OF VISIBILITY METER

DEGRADATION OF PAINTS

G.C. Smith

ABSTRACT

Exposure of paints to the weather causes them to gradually degrade, thus drastically weakening their protective ability. The main factors involved in the degradation processes are water, heat, light and oxygen. The effects of these environmental influences on the molecular structure of the paint are reviewed. It is also shown how molecular changes can affect a paints performance in practice.

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1. INTRODUCTION

A paint film normally consists of a flexible film of solid pigment dispersed in a solid film of polymeric binder. This film is degraded by various environmental influences at a rate which depends on the severity of those influences, the type of binder and the type of pigment and additives in the paint.

Some aspects of these factors, as they affect paint degradation, will be reviewed. Firstly, the effects of temperature, water and abrasion will be described in general terms. The effect of ultraviolet (U.V.) light and oxygen on some commonly used binders, namely, oils, alkyds and vinyls, will then be discussed in somewhat greater detail. Finally, the role of pigments and additives will be examined.

2. ENVIRONMENTAL INFLUENCES

2.1 Temperature

Temperature can affect both the physical and the chemical processes going on in a paint. As the temperature rises the paint becomes softer and less viscous. This change in viscosity can occur suddenly at one particular temperature called the glass transition temperature. Above this temperature a paint is rubbery, flexible and relatively soft, below it is hard, glassy and brittle. This effect is shown in the well known experiment where rubber is dipped into liquid air and becomes hard and brittle and can be shattered like glass.

A paint is usually formulated so that it stays flexible, but not too soft, throughout the temperature range to which it is supposed to be exposed.

However, if the temperature is abnormally high the paint will be softer than normal and if it is abnormally low the paint may go below its glass transition temperature and become brittle. This glass transition temperature can change throughout the paint's life. If the paint becomes harder (crosslinks) as it ages, this may raise the glass transition temperature to a point where, in cold conditions, it may become brittle. For example, as a plastic garden hose ages it loses plasticiser and this raises its glass transition temperature so that it may become brittle in cold weather.

Chemical reactions in a paint proceed faster at higher temperature. In fact a ten degree rise will approximately double the rate of reaction. This effect may be enhanced if the viscosity of the paint is markedly lowered. Such reactions as the breakdown of peroxide groups and hydrolysis of esters are affected this way; these reactions will be discussed later.

2.2 Water

Water can also affect a paint film physically and chemically. If the binder is made up of a polyester backbone, e.g. alkyd or oil based paints, water can react with it (this is called hydrolysis) and break the backbone thus weakening the paint film. If the ester part of the polymer is not in the backbone, hydrolysis will not break the polymer up but will make it more water soluble.

Physically, the water can cause the polymer to soften and swell. Water can also wash away non polymeric materials such as plasticisers and degradation products. All these weakening effects make the paint more susceptible to abrasion by airborne materials. Rain (a common airborne material) causes erosion of paint films and this is especially a problem with the paint on aircraft. Rain softens the paint and at high speeds, abrades the softer paint.

2.3 Light and Oxygen

Light and oxygen usually work in together in a process known as photo-oxidation. This process is a general one, but here it will be described in relation to its effect on oils, alkyds and vinyls.

2.3.1 Alkyds and Oils

Paints based on alkyd resins make up three quarters of the amount of paint used by the services. They are the usual type of solvent based paints used for buildings and structures in non-specialised environments. Most exterior house paints are alkyd paints. Oil based paints have now been largely superseded by alkyds although they are sometimes used in specialised paints e.g. red lead primers.

Alkyds and oils can be discussed together because, in part, they have similar structures and react in a similar way to oxygen, light and water; the main difference is that alkyds contain phthalic anhydride which results in better gloss retention.

These types of paints dry by reaction with oxygen in the air to give crosslinked structures i.e. the original molecules are joined up to make much larger molecules which are solid.

Because oxygen is present all the time this drying process can continue throughout the life of the paint. However, it does get slower and slower because the oxygen finds it more and more difficult to penetrate the solid crosslinked film. Ultraviolet light accelerates this drying process but it also degrades the film once it is formed. When the U.V. light is absorbed by the paint, the energy transferred to the molecules of binder by this absorbtion can be used to break the chemical bonds in the binder. The weakest bond in the dried paint is the oxygen - oxygen bond and so this is the one that receives the brunt of the attack. When this bond is broken it forms radicals which are highly reactive and may attack any molecule near it. This attack can lead to accelerated crosslinking or the radical may break apart and thus weaken the paint film. The processes involved in the drying and U.V. degradation of an alkyd or oil paint are shown in Figure 1. The crosslinking will make the film harder, more brittle and less flexible but if the paint is applied to a surface which does not suffer much deformation e.g. a wall, this alone will not make much difference. However, crosslinking also causes shrinkage of the paint film and this aspect combined with its brittleness may cause enough stress in the paint for it to crack.

If the radical breaks apart it will form smaller molecules which may be volatile or water soluble. In this way the paint film is lost to the environment - the polymer breaks down into smaller molecules which are washed away by rain or evaporate into the air. These evaporating substances give a newly painted surface its characteristic smell.

2.3.2 Vinyls

Solvent based vinyl paints are used to protect steel in corrosive environments. These paints are often based on a copolymer of polyvinyl chloride and polyvinyl acetate with the usual pigments dispersed in them.

Of the vinyl polymers, P.V.C. is the one that is most susceptible to attack by ultraviolet light and this attack is accelerated and continued by oxygen. The main problem with PVC is dehydrochlorination, that is, it slowly loses hydrogen chloride when exposed to the U.V. light. The problem is accentuated by the fact that once some hydrogen chloride is lost it is easier for the rest to be lost. This process forms a string of double bonds which are easily oxidised by air. The degradation then proceeds in a similar way to alkyd oxidation, that is, radicals are formed which can crosslink or break the polymer chain (see Figure 1).

These reactions can be stopped in a number of ways. U.V. absorbers and antioxidants help but are not good enough on their own. Other stabilisers are added which absorb hydrogen chloride or deactivate double bond systems thereby preventing further reaction.

3. ROLE OF PIGMENTS

Pigments perform a useful function in paints besides the obvious ones of hiding power and coloration. They help to physically strengthen the binder and make it less susceptible to environmental attack. Light is absorbed and reflected by pigments and therefore does not have a chance to degrade the binder beneath. Consequently paints which are pigmented last longer than varnishes, which are unpigmented. However, recent work has shown that titanium dioxide (the commonest white pigment) can cause degradation in some circumstances. Although a pigmented film is less susceptible to

degradation than an unpigmented film, when this breakdown does occur it can occur around the pigment particles and seems to be accelerated by these particles.

In the presence of titanium dioxide light can activate a water/oxygen mixture so that a high energy species is formed; this species then attacks the binder which surrounds the pigment particle. Figure 2 shows a diagram of this effect. The pigment is left virtually bare giving the paint a powdery film on the surface - this is chalking.

4. ROLE OF ADDITIVES

Polymers in a paint often absorb some of the ultraviolet (U.V.) light falling on them and it is the absorbed U.V. light which does a lot of damage. However, if an efficient U.V. absorbing compound is added to the paint, even in small amounts, it can effectively screen the U.V. light from the polymer thus preventing the damage. It acts in the same way as many sun tan lotions and in fact the active ingredients of these sun tan lotions have a very similar chemical structure to the U.V. absorbers in paints.

Antioxidants are used in paints as a second line of defence after the U.V. absorbers have failed. Polymers often start their degradation processes by the formation of hydroperoxides and radicals. Antioxidants are designed to harmlessly deactivate the radicals and/or the hydroperoxides. Fortunately, some U.V. absorbers also act as antioxidants so that one compound may serve a dual role.

5. CONCLUSION

An attempt has been made to summarise a few of the more important factors involved in the degradation of paints. The main problem is photo-oxidation of the organic binder of the paint. This is a problem which affects all paints but some of its aspects have been exemplified in relation to three particular resin types namely oils, alkyds and vinyls. The degradation problem can be alleviated to some extent by the correct choice of pigments and additives.

QUESTIONS

R. O'Donnell, W.R.E.

Q. Why does PVC discolour so badly?

A. Double bonds are developed and these absorb more light and are thus highly coloured.

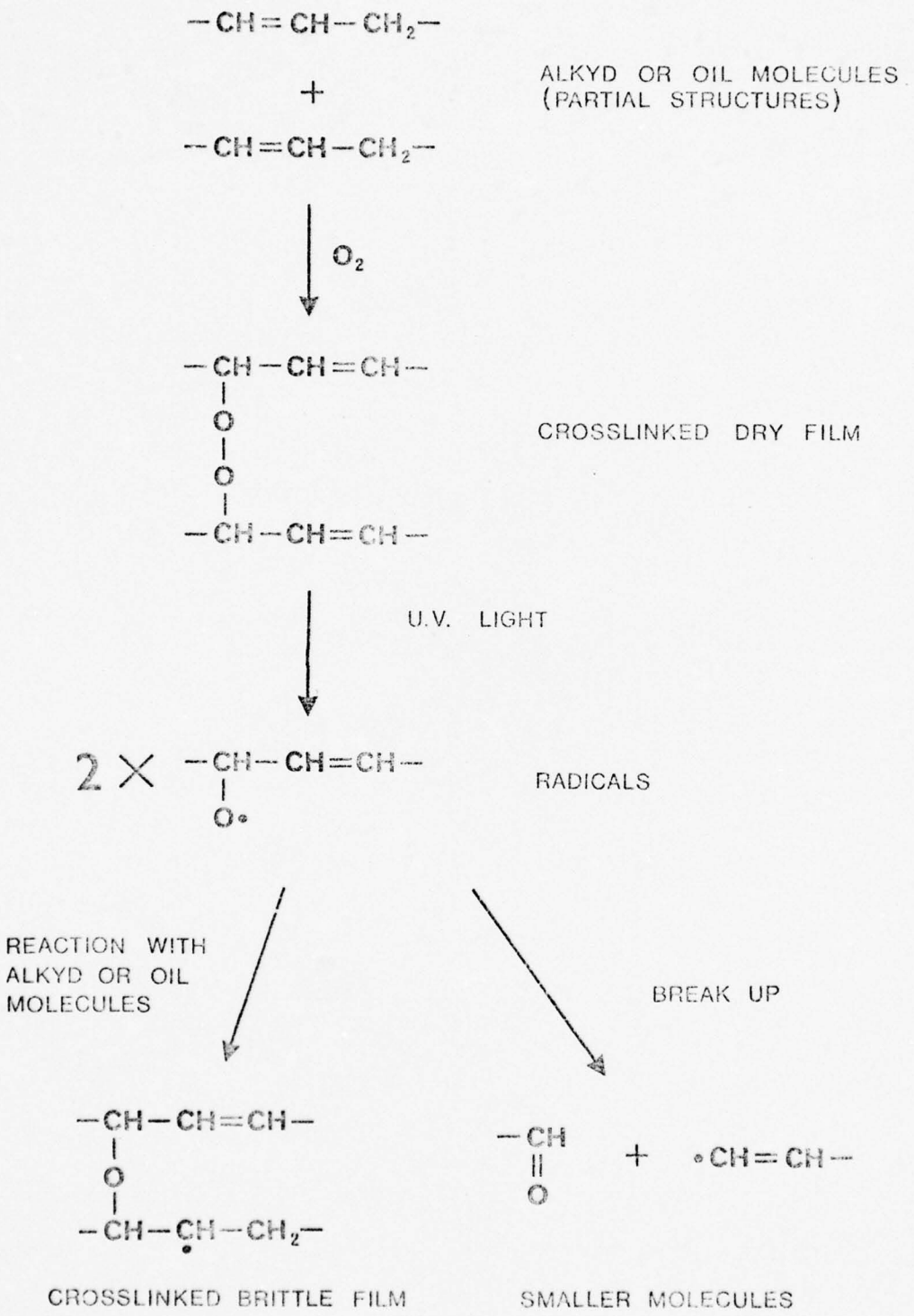
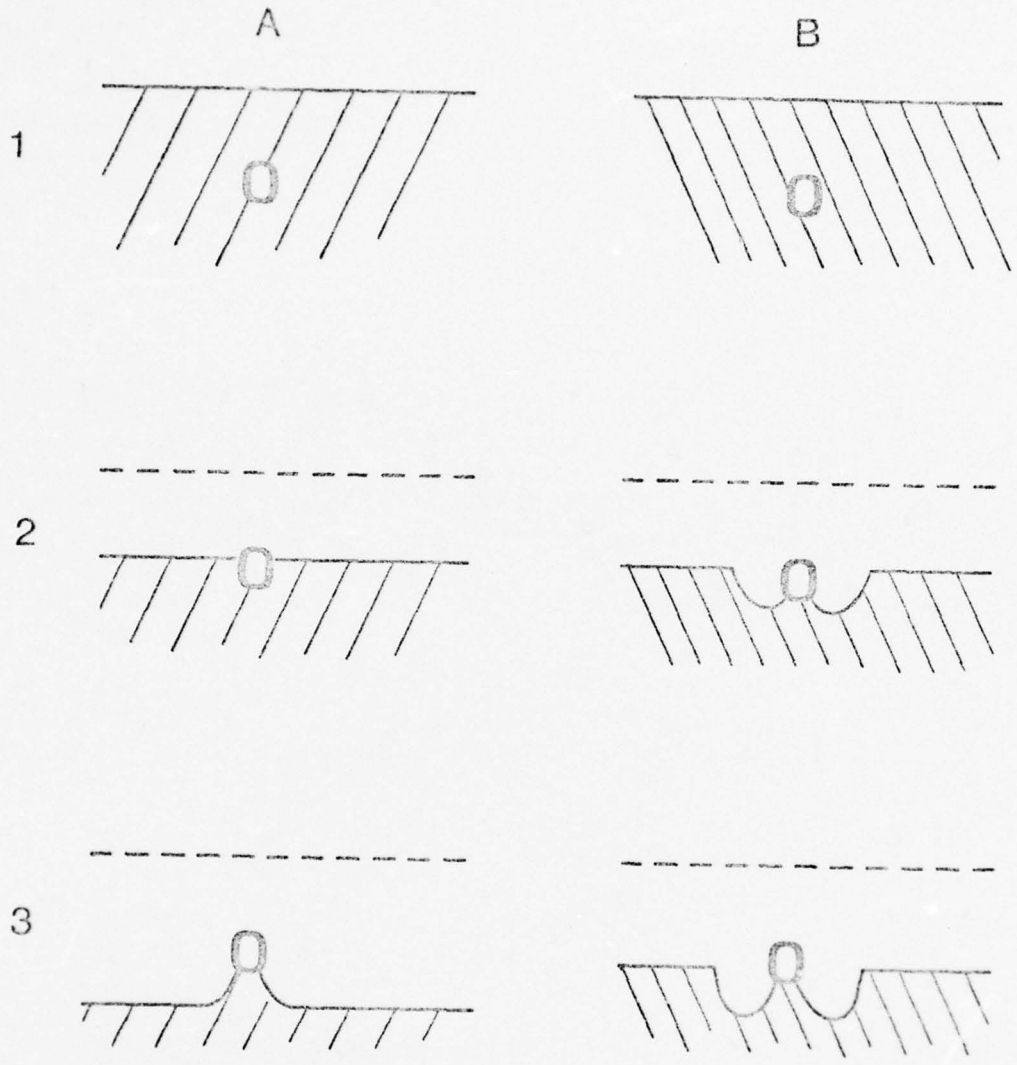

ALKYD OR OIL MOLECULES
(PARTIAL STRUCTURES)
O_2
CROSSLINKED DRY FILM
U.V. LIGHT
RADICALS
REACTION WITH
ALKYD OR OIL
MOLECULES
BREAK UP
CROSSLINKED BRITTLE FILM
SMALLER MOLECULES

FIGURE 1



A. Binder unstable,
Pigment inactive

B. Binder fairly stable,
Pigment active

FIGURE 2

PAINTING OF GALVANISED STEEL

W.N. Hall

ABSTRACT

The reasons for painting galvanised steel are discussed and the various galvanising processes used are described together with the types of surfaces obtained. Details are provided of an investigation into a failure of a paint system on galvanised steel aerial masts. Examination by scanning electron microscopy confirmed that the failure was due to large amounts of loosely bound surface contamination.

The painting of galvanised steel sheet on a production line basis is also discussed. The advantages are mentioned which this material has over the painting of steel galvanised after fabrication.

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1. INTRODUCTION

Over the years there have been many failures of paint systems on galvanised steel which has always been regarded as a difficult material to paint. When new, galvanised steel has a smooth water-repellent surface and many paints tend to lose adhesion from this after a relatively short period of exposure.

The traditional prepainting treatment for galvanised steel is a period of natural weathering, from a few months to a year, until the original bright spangled appearance has been converted to a grey matt surface. Painting problems and recommended painting procedures will be discussed.

2. REASONS FOR COATING GALVANISED STEEL

Galvanised steel is coated for a number of reasons, namely, decoration, identification or warning, camouflage and corrosion resistance. The need for improved corrosion resistance requires some explanation.

Normally when galvanised steel is exposed a tightly bound patina of basic zinc carbonate is formed. This patina is insoluble in water and protects the underlying zinc, thus considerably decreasing the rate of corrosion of the zinc. Therefore, depending on the original thickness of the zinc coatings, the steel can last in non polluted, non marine environments for 30 to 100 years.

However in polluted areas, especially where there are high levels of sulphur dioxide in the atmosphere and therefore the rain water is acidic, two detrimental reactions occur. Firstly, any basic zinc carbonate that forms is dissolved by the acidic rain water and secondly the exposed zinc reacts with sulphur dioxide to form zinc sulphite, which is oxidised to the highly soluble zinc sulphate. An examination (1) of 1½ oz/ft^2 (~50 µm) hot dip galvanised material exposed on a factory roof in Smethwick, U.K. revealed that 60% of the zinc coating had been removed after 7 years. Therefore the remaining zinc coating could not be expected to last for much more than a further year.

By the use of appropriate coating systems the access of corrosive materials to the zinc surface is greatly decreased. A trial in Amsterdam (2) has shown that zinc coating provides a stable base which greatly increases paint life, while the paint film protects the zinc coating. Thus a synergistic situation exists in which the combination lasts considerably longer than the total life of each coating alone. The economic advantages of this duplex system are covered in the booklet "Painting of Zinc Coated Steel", published by the Galvanizers Association of Australia (3).

Another advantage of this system is that when repainting is necessary there is no costly rust removal operation required.

3. GALVANISING PROCESSES AND THEIR EFFECT ON PAINT SYSTEMS

Basically the galvanising process involves the following stages :

(i) Initial cleaning: loose rust, scale, grease etc. is removed by either dipping or spraying with a hot cleaning solution, e.g. caustic or detergent. The article is then pickled in dilute sulphuric acid or hydrochloric acid, thus removing most of the tightly bound rust. A water rinse follows. Castings are usually shot blasted or cleaned electrolytically to remove foundry sand and surface carbon.

An alternative cleaning method used when continuously galvanising steel strip is to pass the strip through an oven in which organic contaminants are oxidised then the strip passes through a furnace with a reducing atmosphere, thus removing surface oxides.

(ii) Fluxing: The pickled article is immersed in a flux solution, usually 30% ammonium chloride with wetting agents, heated to 65°C. The flux solution dissolves and absorbs any remaining impurities, moisture or oxide film to ensure that a chemically clean steel surface is presented to the molten zinc when the article enters the galvanising bath. On removal from the flux solution the article is dried.

An alternative method of fluxing is to place a layer of ammonium chloride on top of the molten zinc. The article to be galvanised picks up the flux as it passes through this layer. This method is going out of fashion because (a) the atmosphere in the vicinity of the bath is filled with ammonium chloride fumes

and (b) when the coated article is removed from the bath it is likely to pick up some ammonium chloride, which is deleterious to the adhesion of any subsequent paint system.

(iii) Galvanising: On immersion in the galvanising bath the steel surface is immediately wetted by the molten zinc and reacts to form zinc-iron alloy layers. To allow formation of the galvanised coating the work remains in the bath until its temperature reaches that of the molten zinc, in the range 445°C to 465°C. The period of immersion varies from a few seconds for continuously galvanised steel sheet to several minutes for massive steel structural members.

The steel article is removed from the bath at a controlled rate and, in addition to the zinc iron alloy layers, it carries a coating of molten zinc which solidifies to give the relatively pure outer zinc coating with its characteristic zinc crystal or "spangle" pattern.

Tin (1%) can be added to the zinc bath to give improved gloss and a uniformly spangled appearance. Aluminium can be added (~ 4%) to improve ductility on sheet that is to be roll formed.

The various types of surfaces that can be obtained are :

(a) Bright spangle or regular spangle: natural crystalline appearance that develops as the molten zinc coating solidifies under rapid cooling.

(b) Minimised spangle: zinc crystals much smaller, obtained by slow cooling of the zinc coating in a steam jet.

(c) Galvannealed: uniform grey appearance, no evidence of spangles, obtained by heat treatment. The heat treatment causes development of a zinc-iron alloy throughout the full thickness of the zinc coating.

Manufacturers suggest that paint can be directly applied to (b) and (c) without treatment other than degreasing while (a) requires a phosphate treatment. Generally the best paint performance is obtained over the galvannealed material.

4. PRETREATMENTS

Galvanised steel is often treated to improve paint adhesion and performance. The most common treatments are :

(i) Hot Phosphate - factory application

(ii) Cold Phosphate - field application

(iii) Hot Chromate - factory application

(iv) Wash (etch) primer.

It was found in a project performed by the Pittsburgh Society for Paint Technology (4) in which hot phosphate and hot chromate pretreatments and wash primers were compared, that in general the order of performance was phosphate, wash primer, chromate. The paints used in this project were epoxy, vinyl, alkyd and acrylic based. The tests performed were water immersion, exposure to high humidity, exposure to salt fog, impact, bend, adhesion, exterior exposure.

5. PERFORMANCE OF VARIOUS COATING SYSTEMS

It would appear that there has not been a detailed program of exposures performed in Australia to determine the performance of various coating systems on galvanised steel. The following information has been obtained from a major paint manufacturer regarding paint systems which are still performing well on a number of structures around Melbourne.

(i) Qantas Cargo Terminal - Tullamarine, degrease/Lithoform/solventless epoxy micaceous iron oxide - 8 years.

(ii) Springvale Migrant Hostel, degrease/Lithoform/Epoxy primer/polyurethane - 4 years.

(iii) SEC Transmission Tower, Yarra river, degrease/alkyd zinc chromate primer/alkyd enamel - 7-8 years.

(iv) S.R.W.S.C. Water tanks Cranbourne and Berwick, zinc metal spray (in place of hot dip galvanising)/Water borne acrylic - 4 years (exterior).

6. INVESTIGATION INTO A FAILURE OF A PAINT SYSTEM ON GALVANISED STEEL

A paint failure occurred recently on some galvanised steel aerial masts manufactured in South Australia. The failure was basically due to poor adhesion of the coating, i.e. it was peeling off. The painting process which was in accordance with DEF (AUST) 3000 (5) consisted of :

(i) Hot caustic dip.

(ii) Cold running water rinse.

(iii) Hot phosphate dip.

(iv) Cold running water rinse.

(v) Hot chromic acid (1-2%) dip.

(vi) Wash primer (30 min at 115°C).

(vii) Alkyd zinc chromate primer (30 min at 115°C).

(viii) 2 coats full gloss alkyd enamel (40-60 min at 115°C each coat)

We considered that it was rather unusual to use a wash primer over a phosphate coating, however since this system had proved to be satisfactory in the past we attempted to determine the cause of this failure.

Initially we prepared test panels using the above system on Galvabond sheet, and found the system to be satisfactory with regard to adhesion. We subsequently obtained some test panels that were galvanised by the firm that galvanised the aerial masts. On coating these panels we observed that the adhesion was significantly inferior to that of the coating on Galvabond panels. We therefore concluded that the surface of the zinc obtained from the firm that galvanised the mast was the most likely cause of the paint failure.

Following on from this work we obtained test panels from three Victorian galvanisers and from the firm in South Australia. We also obtained some weathered Galvabond panels from our branch in South Australia. These panels and panels cut from new Galvabond were degreased and then painted with the systems described in Table 1. After water immersion and humidity testing we found that the adhesion of the systems that incorporated water based systems was vastly superior to that of the systems where alkyd paints were incorporated. However after artificial weathering we observed that, although the acrylic systems generally had superior adhesion to the alkyd systems, the adhesion of systems C, J and K was good. The results from the accelerated weathering tests also showed that the performance of most of the paint systems was worst over the S.A. manufacturer's galvanised steel.

However the results of adhesion tests after 18 months exterior exposure (see Table 2) show that only in the case of three paint systems is the adhesion significantly worse on the S.A. manufacturer's galvanised steel than on all other surfaces. These systems were zinc dust-zinc oxide primer/alkyd (System A), etch primer/zinc chromate primer/alkyd (System C) and galvapren/zinc chromate primer/alkyd (System J). We have examined the zinc surfaces using scanning electron microscopy, and have found that the S.A. manufacturer's material is the only one that has large amounts of loosely bound surface contamination.

These short term results indicate that the water based systems are least likely to fail on galvanised steel. This is not surprising because it has been shown by Bullett (6) at the Paint Research Station in U.K. that zinc formate which causes loss of adhesion, can be formed at the zinc-paint interface when alkyd paints are applied to zinc surfaces. The reason given for the formation of the zinc formate is that small amounts of formic acid are produced by the oxidation of the fatty acid in the alkyd resin; this formic acid migrates through the paint film and reacts with the zinc surface forming zinc formate.

No such decomposition occurs in the resins, e.g. acrylic used in water based paints.

7. COIL COATED GALVANISED STEEL

I would now like to mention briefly coil coated galvanised steel, that is galvanised steel sheet that is painted on a production line. There are a number of commercial materials of this type available. The coatings are selected so that they have sufficient flexibility to endure without damage subsequent mechanical operations, e.g. roll forming, stamping and pressing. The types of coatings that can be obtained are acrylics, alkyds, vinyls, silicone polyesters and epoxies.

TABLE 1

DESCRIPTION OF PAINT SYSTEMS

		Systems											
		A	B	C	D	E	F	G	H	J	K	L	M
PRETREAT	Nil	x	x		x	x	x						
	Etch Primer			x									
	Galvaprep 10							x	x	x	x	x	x
PRIMER	Berger Zinc Dust/Zinc Oxide-Alkyd	x	x					x	x				
	Berger Zinc Chromate-Alkyd			x						x			
	Dulux Galv. Iron Primer Water-based				x	x					x	x	
	Dulux Spruce-Acrylic Water-based (Now Weathershield Gloss)						x						x
TOPCOAT	Dulux Hi Gloss-Alkyd Enamel	x		x	x			x		x	x		
	Dulux Spruce		x			x	x		x			x	x

TABLE 2

ADHESION OF PAINT SYSTEMS TO GALVANISED STEELS

AFTER 18 MONTHS EXTERIOR EXPOSURE

Paint System	Galvanised Steel					
	Galvabond	Galvabond Weathered	S.A. Manufacturer	Vic. Manufacturer (1)	Vic. Manufacturer (2)	Vic. Manufacturer (3)
A	130	170	10	140	105	100
B	200	170	150	168	100	175
C	205	190	115	200	200	190
D	85	90	40	25	80	45
E	240	260	235	80	250	170
F	250	215	200	200	220	185
G	230	260	190	200	190	185
H	150	200	150	160	185	180
J	85	75	30	70	85	65
K	80	150	185	165	155	160
L	200	235	190	200	185	135
M	230	225	250	140	160	200

Adhesion values are in kgf/cm^2

The coating operation consists of cleaning (alkali detergent) with abrasion (scotchbrite), pretreatment (zinc phosphate) coating one or two coats (roller coating) then stoving, air cooling, water quenching then drying. Line speeds of 110 m/min can be obtained.

The advantages of this material over the painting of galvanised steel after fabrication are :

(i) The control of these lines gives a quality of finish that would be very difficult to obtain by post painting.

(ii) Painting facilities are either unnecessary or decreased in scale, thus saving on capital investment and pollution control.

(iii) The coatings have inbuilt lubricating properties which protect tool faces during fabrication.

The main disadvantage of this type of material is that during fabrication care is needed to ensure that the coating is not damaged.

Some of the uses of this type of material are wall cladding, roofing and guttering, appliances, acoustic tiles, furniture, cool room panels, highway signs, shelving, instrument panels, bus bodies, garage doors.

QUESTIONS

J. Schweitzer, D.Q.A. Air

Q. Is it satisfactory to weather galvanised steel before painting?

A. This is satisfactory in rural and suburban areas but not in polluted or coastal areas where soluble zinc salts are formed on the surface.

R. Pettis, M.R.L.

Q. How do you define a polluted area?

A. The concentration of atmospheric sulphur dioxide would be the most important factor. I do not have the information necessary to define the borderline between polluted and non-polluted areas.

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FUNGI AND MATERIALS

F.J. Upsher

ABSTRACT

Microfungi are the most important single group of biodeterioration organisms. Provided moisture is present, they can grow under a variety of conditions and attack many organic compounds and materials through the release of extracellular enzymes. Most naturally occurring substances and certain man-made materials, notably the polyesters, are susceptible to attack but many are resistant. The incorporation of a susceptible component can render the whole complex susceptible but the material can be protected by incorporating an appropriate biocide which will also prevent superficial microbial growth.

1. INTRODUCTION

Fungi, particularly the microfungi, are the most widespread and destructive single group of micro-organisms encountered in biodeterioration. Bacteria, Actinomycetes, Cyanophytes, Algae and Lichens are also involved but their effects are generally overshadowed by the destructive action of the fungi. Microfungi have evolved so that they are active in the natural decomposition of organic debris to carbon dioxide. As a group they are thus equipped to attack almost all naturally occurring macromolecules and a number of synthetic materials too.

In plastics, rubbers, paints etc. the polymer matrix or some other component may be attacked, resulting in loss of flexibility or toughness. Paints and other surface coatings are also liable to spoilage through disfigurement. Microfungi derive nutriment not only from the coating but also from debris and other surface deposits. Algae also cause disfigurement of paints and other decorative finishes in humid situations.

2. MICROFUNGI AND FACTORS INFLUENCING THEIR GROWTH

Microfungal colonies are made up of branched hyphae (10 μm in diameter) and produce spores often in vast numbers by which the species are propagated. The spores are generally carried by air movements, so that any surface exposed to the atmosphere will become contaminated.

All micro-organisms are dependent on water for growth but microfungi can not only utilize free water but can derive sufficient from atmospheric moisture when the relative humidity exceeds about 75%, growth being faster at higher humidities. On the other hand they are also tolerant of being dried, when they become dormant. Fungi present on surfaces exposed to the tropical sun can be baked every day yet resume growth when wet with dew at night.

As a group they grow between $0^{o}C$ and $55^{o}C$, the range of temperature through which any species can grow is about 25^{o}. In temperatures above the

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maximum for growth, they die. The higher the temperature the quicker they die. The rate of death depends on a number of factors, the main one being water content of the cells with dried cells being more resistant to heat than fully hydrated cells. In temperatures below the minimum of the growth range they become dormant, but resume growth with the return of favourable conditions.

Many fungi are pale coloured or colourless and these generally prefer shaded environments but in others - the dematiaceous types - the cell walls contain melanoid pigments which protect the contents from the otherwise lethal ultraviolet radiation. This enables several genera including Alternaria, Aureobasidium, Cladosporium, Curvularia and Nigrospora to grow on paints, plastics etc. exposed to the tropical sun.

Microfungi are generally tolerant of a wide range of pH, growing between pH2 and 10, often with optima between 4 and 7. They absorb their foods, in solution, through the cell membrane which lines the cell wall. Their mineral requirements are satisfied by a small number of elements. Potassium and magnesium are absorbed as the cations, nitrogen is taken up as nitrate or ammonium ions, sulphur as sulphate and phosphorus as phosphate. These elements may also be absorbed as organic compounds. Also necessary but in minor quantities, some less than 1 ppm in solution, are trace elements including iron, copper, manganese, molybdenum, zinc, nickel and boron.

The organic nutrition of microfungi is less simple. They are heterotrophic, i.e. they require organic compounds to provide energy and for the generation of new cellular material. Sugars, amino acids and other water soluble molecules are readily assimilated but microfungi, like the actinomycetes and bacteria also obtain nutriment from larger, insoluble molecules. To catalyse the necessary breakdown they excrete quantities of enzymes, many of which are hydrolytic e.g. glycosidases, amidases and esterases, but others catalyse oxidative and reductive actions. The nett result is invariably that a part of the original insoluble molecule is split off, frequently a 2-carbon unit from a chain end, yielding a water-soluble product. It is because of this ability to degrade organic compounds that the microfungi are destructive towards a variety of manufactured materials.

3. MATERIALS AND THEIR SUSCEPTIBILITY

It is convenient to divide materials into two categories, natural and manufactured, and those of natural occurrence according to their origin. In materials derived from plants the structural component is cellulose, accompanied by varying quantities of lignin. Cellulose is rapidly broken down by microbial ß-glucosidases (cellulases) but lignin is more resistant to enzymic attack. Fibrous materials of animal origin such as wool, silk and leather are all proteinaceous and are readily attacked by peptidases (amidases). However, these materials have been developed through evolution to protect the animal beneath and have greater resistance to enzymic attack.

Almost all of the other naturally occurring substances including the polyisoprene component of natural rubber and various oils, waxes, starches and glues etc. are susceptible to attack by microbial enzymes.

It is convenient to place those naturally occurring materials which have undergone severe chemical modification such as the substituted celluloses and epoxidised oils in the same category as the man-made materials which include paints, plastics, rubbers and adhesives. A feature common to all of these is that none is a pure homotype. All contain either traces of monomer, oligomer or some oxidation or breakdown product, or are intentional mixtures of a polymer matrix with various additives such as fillers, plasticizers, anti-oxidants, catalysts, blowing agents, dyes, pigments and UV absorbers. With such variety of ingredients, some of which are susceptible to attack, the resistance of a material to fungal attack is very much determined by its formulation, as may be seen in the three basic causes of microbial attack that can be distinguished, namely:

1. The polymer is susceptible

2. The polymer is resistant but some other component is susceptible

3. All components are resistant but surface deposits or substances nearby are susceptible.

Laboratory tests have enabled polymers to be classified according to their susceptibility as shown in Table 1. However because of the heterogeneity of polymers the classifications are not absolute.

TABLE 1

Susceptibility of Polymers to Microbial Attack

Susceptible	Variable	Resistant
Polyester polyurethanes (4)	Formaldehyde resins (5,6)	Polyolefins (5,6,7)
Naturally occurring polymers	Substituted celluloses (5,6)	Substituted polyolefins (7)
	Polyesters (7)	Polyamides (5,6,7)
	Polyether polyurethanes (4)	Polyvinyl resins (5,6)
		Acrylics (5,6,7)
		Synthetic rubbers (7,8,9)
		Polycarbonates (5,6)
		Epoxy resins (5,6)
		Polystyrene (5,6,7)
		Polysulphides (8)
		Silicones (5,6,8)

In polyethylene, for example, the small polymer molecules, MW ~ 500 which are susceptible to microbial growth and are present in most polyethylenes with mean MW up to about 20,000, account for the apparent susceptibility of that material (7,10).

Although the vinyl resins are uniformly resistant to attack, growth on poly vinyl acetate is believed to be associated with the presence of free acetate (11).

The group of formaldehyde resins includes several which are essentially resistant (phenol formaldehyde, recorcinol formaldehyde, urea formaldehyde) and some which are susceptible (phenol aniline formaldehyde, casein formaldehyde). Conflicting reports have been issued on the resistance of melamine formaldehyde (5,6).

Although cellulose is a naturally occurring polymer and is itself highly susceptible to enzymic attack, its resistance can be varied by chemical substitutions. Cellulose-butyrate, cellulose-acetate-butyrate, cellulose-acetate-propionate, ethyl cellulose and cyanoethyl cellulose are all resistant. Cellulose mono-acetate has a low resistance but this increases with further acetylation. Notably reconstituted celluloses, such as rayon, are susceptible (5,6).

The resistance of poly-ether polyurethanes depends largely on the type of diol present. Those containing low molecular weight, unbranched alkane diols such as 1,4-butane diol, and 1,6-hexane diol and the higher molecular weight propylene glycols (MW 1000-3000) tend to be susceptible, attack occurring where there is a sufficiently long unbranched carbon chain between urethane linkages (3).

Polyester-type polyurethanes and certain other polyesters are unusual among the synthetic polymers in that many of them are readily broken down by micro-organisms. The ester bond can be attacked by microbial esterases and either or both the acid and alcohol groups may be further broken down to provide nutriment for microfungi. Despite their susceptibility, polyesters and particularly polyester polyurethanes have gained widespread applications, and consequently, there have been many reports of their biodeterioration (3,4,12,13,14,15).

In the second form of biodeterioration, where the polymer matrix is essentially resistant to attack but some other component is susceptible, greatest influence is exerted by susceptible components present in the greatest proportions - such as fillers and plasticizers.

Mineral fillers such as silica, clay and carbon black, glass and asbestos are inert and do not support microbial growth but organic fillers such as wood flour may make up as much as 50% of a thermosetting formaldehyde resin rendering the whole composite susceptible.

Microbial attack of plasticizers such as those in certain vinyl and other plastics results in loss of flexibility and elasticity and greater

hardness. Many plasticizers are of the ester type and although the vulnerability of these substances has long been recognised they continue to be used. Certain non-ester plasticizers are also susceptible (Table 2).

The susceptibility of ester-type plasticizers like the polyesters, stems in part from the easily hydrolysed ester bond, though the degree of susceptibility may be modified by the spatial configuration of adjacent groups, particularly by the acid component, certain acids tending to confer resistance and others being themselves easily degraded (Table 2).

TABLE 2

Susceptibility of Plasticizers to Microbial Attack

	Resistant	Susceptible
Esters	Aconitate (16,17)	Adipate (16,18,19)
	Citrate (16,17)	Azelate (16,18,19)
	Maleate (16,18)	Laurate (16)
	Phosphate (16,17,19)	Oleate (16)
	Phthalate (16,18,19)	Ricinoleate (16,17)
	Toluene sulphonate (16)	Sebacate (16,17,19)
		Stearate (16,18)
		Succinate (16,19)
		Some Alkyl esters (6,16,20)
Others	Aromatic hydrocarbons (16)	Glycerol (6,16,18)
	Chlorinated hydrocarbons (6,16)	Pentaerythritol derivatives (6,16)
		Poly-ethylene glycols (18)
		Epoxidised oils (19)

The configuration of the alcohol group also influences the susceptibility of an ester (20). Attack of the alkyl chain in alkyl esters is hindered by chain branching because chain breakdown proceeds by a β-oxidation process which removes carbon atoms in pairs. Consequently 1.3-dimethylbutyl- and 2-ethylhexyl-esters are more resistant than the corresponding n-hexyl- and n-octyl-esters respectively. This blocking

mechanism is common to other carbon chains and cross linking has the same effect, as in polyethylene, rubbers, polyurethanes, and petroleum materials (21).

The third form of biodeterioration is that in which no part of the material is susceptible but organisms grow over the surface, deriving nutriment from surface deposits or adjacent materials. Deposits of any origin containing sufficient available organic matter will support fungal growth-dust, aerosols, condensates, fingerprints, spider web threads or substances deliberately applied such as spinning and weaving aids in textiles and cutting aids on polyurethane foams. Products of oxidation or other breakdown may form a surface layer which can also support growth.

This type of deterioration is a particular problem with paints and other surface coatings since they are often employed for long periods in situations where debris and condensates can accumulate, providing microbial nutriment and retaining moisture to favour growth. Whatever the origin of the deposit, the apparent result is the same but superficial growths must be distinguished from those associated with attack of the material.

Examples of this type of deterioration include the etching of optical lenses by fungi which derive their nutriment from the adjacent luting or from deposits on the lens, fungi in aircraft fuels penetrating the tank linings and causing corrosion and perforation of the alloy tanks, and the fungal penetration of silicone gums.

4. PREVENTION OF FUNGAL GROWTH

To prevent microbial growth by control of environment is not generally practicable but the principle is applied where a dry atmosphere can be maintained such as in store rooms and in the sealed enclosures of new goods. Materials and equipment can be made which are resistant to microbial attack by incorporating only materials known to be resistant but then would still be liable to surface growth of micro-organisms. In many applications such as decorative surfaces, marine finishes and in electronic and optical equipment, any such growth is unacceptable. In cases where no fungal growth can be tolerated or where it is otherwise expedient to use a material known to be susceptible growth can only be prevented by incorporating a suitable biocide. As a greater variety of more effective biocides become available, better protection can be afforded, but selection becomes more involved. A number of factors have to be considered. At an effective concentration, the biocide should not

(i) impair the physical properties of the material

(ii) catalyse oxidation or other degradatory action

(iii) be volatile or produce an undesirable odour

(iv) be toxic to man, animals or the environment

(v) cause corrosion or other spoilage of adjoining materials

(vi) be leached by water (or other solvent)

(vii) become inactivated under the conditions of service of the material during the anticipated service life.

Although our present knowledge of materials, of the chemistry of microbial attack and of methods of controlling microbial growth is adequate to ensure the durability of a material, micro-organisms are sufficiently tenacious and versatile to continue to cause problems.

QUESTIONS

J. Baker, A.F.F.

Q. What action would you recommend after microbiological attack has occurred on a paint surface.

A. Cleaning the surface with a detergent and then wiping over with a bleach solution to given an improvement in appearance but if real damage has occurred, repainting could be necessary. Then you would use a paint containing a fungicide.

R. O'Donnell, W.R.E.

Q. What is the resistance of polyurethanes?

A. Polyester polyurethanes are all regarded as susceptible. Resistance of the polyether types would depend on the diol present.

W. Hall, M.R.L.

Q. How are tents protected nowadays from attack in the tropics.

A. Mostly with copper 8-quinolinolate: organotins are also being introduced.

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COATING PROBLEMS IN THE SERVICES

PART I (NAVY)

B. Wearne

ABSTRACT

The problem areas of particular interest to the Navy are discussed. These include:-

(i) exterior underwater items such as rudders, sea tubes and sonar trunks

(ii) radar antennae whose design often makes preservation difficult

(iii) general machinery spaces and associated problems of corrosion in inaccessible areas

(iv) ballast, fuel and fresh water tanks for which adequate surface preparation is often difficult thereby precluding the use of heavy duty coatings

(v) ventilation trunking and magazine decks.

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1. INTRODUCTION

The problems encountered in corrosion protection on RAN ships can be divided into two broad areas, namely exterior and interior surfaces. This broad division is appropriate because of differences in the environment and accessibility for surface preparation and painting.

2. EXTERIOR SURFACES

2.1 Wind and Waterline

In these areas, abrasion damage occurs due to rubbing by waterline fenders and other floating objects. Any corrosion that is initiated because of this action, will be accelerated due to the intermittent immersion caused by wave action.

2.2 Underwater

At the bow section, heavy abrasion is caused by chafing of anchor cables.

Early stripping of paint on rudders invariably occurs due to turbulence set up by high speed propellers followed by cavitation corrosion on the subsequently bared rudder surfaces.

Sea tubes and sonar trunks present problems because of limited access which prevents adequate preservation, and the presence of large bronze valves etc., gives rise to dissimilar metal corrosion.

The coating system normally used in the above areas is an aluminium bituminous barrier coating overcoated with antifouling paint. Other more sophisticated coatings such as coal tar epoxies have repeatedly failed, and in any case maintenance problems are increased by their use.

2.3 Above Water

Radar antennae some of which are constructed of high copper aluminium alloy, are always a problem in corrosion control, due to their continual exposure to corrosive funnel gases as well as salt spray and sunlight. Quite often they are of a complex design that renders adequate maintenance difficult. The choice of coatings may also be restricted because of the necessity not to interfere with the R.F. properties of the radiating and receiving surfaces. Chlorinated rubbers have been used in this application with some success, but they do require good surface preparation.

Channel plating carrying electric wiring is also prone to corrosion because of the slotted plate design and inaccessible siting.

Guard rail stanchions and stays are being made from aluminium to an increasing extent and must be adequately protected against corrosion and abrasion. Nylon powder coatings have been used in this area, and while their abrasion and corrosion resistance are quite good, the temperature at which they are applied adversely affects the mechanical properties of the metal.

Group exhaust valves on submarines present a particularly nasty problem in protection as they reach a fairly high temperature in operation (150^{o}) which falls rapidly when the submarine submerges. A number of heavy duty coatings have been applied, but invariably they strip off due to thermal shock.

3. INTERIOR SURFACES

Naval Ships, for reasons of economy and efficiency require that every available space be occupied by some useful piece of often complex equipment necessary for the proper operation of a modern fighting ship.

Because of the ensuing inaccessibility of many areas within the hull structure, maintenance is often extremely difficult if not impossible in service, particularly in submarines. It is only during refits when large items of equipment may be removed, that maintenance is possible. In the machinery spaces, surfaces become contaminated with salt water, oils of various kinds, boiler treatment chemicals, etc., besides being exposed to conditions of high humidity and extremes of temperature both high and low. Certain corrosion problems in this area are enhanced by the presence of large non-ferrous components in direct proximity to the main steel structure of the ship.

Storage tanks, which may contain such things as salt water, fresh water, fuels, and distilled water (boiler feed and potable) are a problem in corrosion control, mainly due to their internal geometry. In many cases it is a physical impossibility to carry out adequate surface preparation prior to the application of a suitable coating. Of course, the only suitable coatings in these areas are the well known heavy duty coatings, but these require the surfaces to be abrasive blast cleaned to the requirements of AS CK 3 Part 4, Class 3 prior to application.

Bathrooms, toilets, laundries and galleys are a problem because of continual exposure to moisture, soaps and other cleaning chemicals, and germicides.

Ventilation trunking, which may be either aluminium or galvanized iron, carries salt laden air to all parts of the ship and is generally of great length and complex configuration. It may frequently contain salt water pools at low spots, the water having entered through the intake and exhaust apertures. Frequently they are of too small a size to render proper internal preservation possible.

Magazine decks may present problems, since certain walkway areas are required to be electrically conducting to eliminate danger of sparking. In the past it was the practice to coat with a zinc rich paint in the belief that it was electrically conducting, but there is now considerable doubt as to whether this is true. Air conditioned missile control rooms have been found to have corrosion on control installations due to heavy condensation occuring after the air conditioning has broken down. Heavy coatings may be restricted here because of the fine tolerance required in the dimensions of certain components.

COATINGS PROBLEMS IN THE SERVICES

PART II (ARMY)

R.M. Jones

ABSTRACT

The protective coatings applied to a wide variety of items in service with the Australian Army are required to withstand severe and changeable environmental conditions. The factors which influence the selection of a particular surface coating for application to Army equipment are described.

Three examples are given of items of Army equipment to which protective coatings have been applied and the nature of the specialised requirements which the surface coatings have to satisfy are indicated.

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1. INTRODUCTION

A wide range of equipment used by the Army requires protection against the ravages of corrosion and there can also be the additional need to apply a surface coating for camouflage purposes. The equipment may be used or stored for long periods under harsh environmental conditions which requires a coating with superior properties in order to obtain effective protection.

The two major factors which would normally influence the selection of a protective coating for Army equipment are:

(a) ability to provide the required protection under the expected environmental conditions;

(b) suitability for use in refurbishing equipment, under active service conditions, to prolong service life.

2. COATING REQUIREMENTS

2.1 On Leopard Tanks

One of the Army's latest and perhaps its most expensive piece of equipment is the Leopard Tank. The Department of Defence is currently purchasing 53 tanks at a cost of almost $50M. To assess the tank's performance under the conditions it has to withstand during its service life, performance trials were conducted at the Department's Tropical Trials Establishment at Innisfail Queensland in 1974. The trials area was located in a hot humid climate and had available both abrasive saline conditions found in coastal areas, together with the wet humid conditions of the tropical jungle. The tank's amphibious qualities were adequately tested in the many rivers throughout the area and its traction and stability thoroughly assessed in the heavy red clay mud areas. Whilst performing in this type of environment, the tank's protective surface coating was subjected to extreme weathering and rough usage conditions and was required to remain firmly adherent and functional.

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In addition to providing protection against the elements, the coating must provide effective camouflage against infra-red detection plus what may become an increasingly important aspect of all field store coatings, i.e. its ability to resist the effect of chemical warfare agents and any subsequent decontamination process. The coating must be such that it permits the minimum amount of absorption to ensure that, after decontamination, toxic vapours are not retained for later release. The decontaminants used are usually strong chlorine bleaches, and the coating used must be capable of resisting their corrosive effects.

The paint system being used to protect the tank as supplied is a German material about which little is known apart from the fact that it is a two pack epoxy system. If the material were to be manufactured in Australia, the general Australian Army requirement would be that the coating should be:

(a) resistant to chemical warfare agents;

(b) capable of decontamination;

(c) infra-red reflective;

(d) suitable for field use in binary spray equipment.

Ultimately there may be a need to coat all field equipment with this material.

2.2 For Use with Foodstuffs

To illustrate the diversity of Army requirements, we will consider the case of a potato chipper which, by way of our combined Defence role, was in service on HMAS Melbourne. This small but no less important item had the special coating requirements to provide protection against the severe corrosion condition of salt water together with compatibility with foodstuffs. The current item has a nickel coating which broke down to the point of making the item unserviceable after a period of two months.

This example serves to illustrate the importance of selecting the correct coating for the task. Coatings which perform very well under one set of condition may fail badly in a different environment. A new version of this item will be made of cast iron and will require an organic coating which will provide protection against the severe corrosive conditions as well as being compatible with foodstuffs.

2.3 For Mine Trip Wires

Another item with an important and exacting role is the Mine Trip Wire. In addition to the normal IR reflectance characteristic of the coating, extended weatherability is required together with insect and fungus resistance since the mines can often remain in position for a considerable time before functioning.

There is also a need for the coating to be very flexible and firmly adherent, since the wire must be of small section to limit visibility and be capable of being tied and wound.

3. CONCLUSION

These few examples illustrate the variety of coating problems confronting the Australian Army and the type of conditions which the coatings are expected to withstand.

Liaison and feedback of information between the design and quality assurance authorities and the users of service equipment is necessary in order to develop the optimum surface coating.

COATINGS PROBLEMS IN THE SERVICES

PART III (AIR)

W/Off. C.V. Hart

ABSTRACT

Some of the problems arising from the use of epoxy primers and polyurethane finishes on RAAF aircraft are described. Particular subjects discussed include the removal of coatings, repair of damaged or replaced surfaces and reconditioning of existing coatings. The possible use of polysulphide primers is discussed. Another area where problems have arisen is in the application of erosion resistant systems to the leading edges of aircraft.

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1. REMOVAL OF ORIGINAL COATINGS

The removal of epoxy and polyurethane coatings from aircraft periodically becomes necessary for various reasons. The more common reasons are:

(a) deterioration of coatings;

(b) inspection and crack detection; and

(c) corrosion detection and removal.

However the development of more sophisticated surface finishes creates problems in the removal of these coatings. Paint strippers are chosen for their removal efficiency and more importantly freedom from harmful effects on aircraft surfaces. To ensure that there are no harmful effects there is a strict requirement for the strippers to be free of corrosive properties and free from properties capable of inducing hydrogen embrittlement in high strength steels. It is becoming increasingly difficult to remove the vastly improved materials that are becoming available and work is in hand in this regard. Test panels of all the current aircraft paint systems are being prepared. These systems are:

(a) Nitro-cellulose finishing scheme.

(b) Acrylic modified nitro-cellulose finishing scheme.

(c) Epoxy polyamide finishing scheme (epoxy primer - epoxy topcoat).

(d) Polyurethane finishing scheme (epoxy primer - polyurethane topcoat).

(e) Acrylic lacquer finishing scheme (epoxy primer - acrylic topcoat).

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When the test panels have been prepared, manufacturers samples of removers will be obtained and tests carried out in accordance with RAAF Technical Requirements Specification No. K55 to determine their efficiency.

There has also been some discussion in relation to layer removal, which involves the removal of the topcoat without harmful effect to the primer. If this type of paint removal could be successfully accomplished, and the primer conditioned to accept reapplication of a suitable topcoat, it would be acceptable in circumstances where corrosion was not visibly evident and the surface only is in a deteriorated condition.

2. REPAIR OF DAMAGED OR REPLACED SURFACES

The detailed procedure involved in the repair of damaged, and the repainting of replaced, panels in epoxy and polyurethane finishing schemes is a lengthy task. The resultant finish on aged surfaces, when repair or replacement is carried out, has a patchy appearance due to the necessity to mask and paint all repairs in sections. This destroys the aesthetic appearance of the paint finish. As for lacquers where surface blending of materials is possible with the use of solvents, materials for the blending of polyurethanes could be investigated.

3. RECONDITIONING OF COATINGS

The reconditioning of polyurethane coatings by the use of suitable solvents would create a surface that could be recoated by application of polyurethane over polyurethane. This could allow for a considerable saving of time and material over the currently employed system where a keycoat primer is necessary to obtain optimum adhesion.

4. POLYSULPHIDE PRIMERS

The use of polysulphide primers as an alternative to epoxy polyamide primers is being considered. It is believed that these primers will give a superior protection against corrosion than those types of primers currently used within the RAAF. Samples are being procured and testing will be undertaken to assess their value.

Their use would be of interest, particularly in areas such as fastener lines and walkway areas where heavy foot traffic is likely. It should be determined whether the polysulphide primer should be used as a general primer or only on those areas prone to movement and foot traffic. In addition the use of polysulphide primer directly over the conversion coating should be investigated. Considerable work will be necessary before standardization is achieved.

5. EROSION RESISTANT COATINGS

The satisfactory painting of leading edges remains a problem area. The RAAF is currently using an epoxy polyurethane system which replaced a polyvinyl chloride (PVC) plastic film. The current system has been far superior to the PVC plastic film but it still has problems.

The cause of polyurethane paint peeling from the leading edges of aircraft has been shown in most cases to result from one or both of the following practices.

(a) Improper surface preparation and/or the use of incorrect paint application procedures.

(b) Flying through heavy rainstorms which even at moderate speeds can severely damage leading edge paint. Properly applied paint will suffer small pits from rain erosion but improperly applied paint will peel off in large patches (sometimes within 15 minutes) while flying through a heavy rainstorm.

The use of polyurethane tape has some merit although we would prefer to use a superior anti-abrasive system of polyurethane paint. Possibly application of a polysulphide primer with a polyurethane finish could be the answer.

Field evaluation is currently being undertaken of a polyurethane coating system to replace erosion resistant elastomeric coatings to airborne radomes. It is possible that testing of several such materials could be required at a later date.

GENERAL DISCUSSION

F. Marson, M.R.L.

Q. What would the Services consider to be their major problem?

R.H. Jones, D.A.Q.A. Army

A. I consider that you could narrow it down to ease of application. The Army wants durable coatings that can be maintained without too much difficulty.

B. Wearne, G.I.N.D. Navy

A. The major problem in the Navy is in ballast tanks which, due to inaccessibility, are very difficult to prepare adequately for painting.

W/O C.V. Hart, H.Q.S.C., R.A.A.F.

A. Our major need is for a removable and repairable top coat system over a non removable permanent anti-corrosive primer. Cracking at rivets due to inflexibility of finishing coats is another major problem.

J. Kennedy, A.M.R.B. Navy

Q. We have been attempting to obtain supplies, without success, of Solar heat reflecting paints for use on Helicopters. Do you know of a source of supply?

L.A. Hill, M.R.L.

A. We have commenced to make up samples.

COMMENT

R. O'Donnell, W.R.E.

We have done some work in this area using imported material from Pinchin and Johnson, U.K. and local Vessey's material.

L.A. Hill, M.R.L.

Perhaps Mr Kennedy could get in touch with Vessey's and if he wished we could assess the materials from Vessey's against our own.

QUESTIONER

Q. Has a comparison been carried out of the durability of acrylics against polyurethanes for aircraft use.

Mr C. Grey, M.R.L.

A. Yes, we have carried out a comparison and found that there was little difference in the durability of the two materials.

COMMENT

L.A. Hill, M.R.L.

Although there was not any great difference in their durability, there were differences in their fuel resistance and other properties.

J. Kennedy, A.M.R.B. Navy

Q. Reverting to the matter of repairable top coats, would you agree that the epoxy primer/acrylic finishing system would be best.

L.A. Hill, M.R.L.

A. Yes, I agree, this system is being used overseas in both commercial and military applications.

R.M. Jones, D.A.Q.A. Army

Q. Could suitable paint systems be developed for armoured fighting vehicles?

L.A. Hill, M.R.L.

A. Suitable repair coatings for Leopard tanks could no doubt be developed using epoxy materials. Work would need to be done in respect of infra-red reflectance, compatability of system and abrasion resistance.

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