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Avoiding paint failures by prohesion

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Transactions and Communications Reflection measurements on synthetic silica products

By D. Koth and H. Ferch

Degussa, Application and Technical Service Department, Hanau/Main 11, Germany

Summary

Concepts such as 'brightness', 'brightness reference value A' and 'whiteness index' are often used incorrectly or in a manner leading to errors. For this reason, these important concepts are defined below.

On the basis of extensive measurements made on synthetic silica

Keywords

Raw materials for coatings

extender pigments

silica silicate synthetic silica products, the colorimetric values of various groups of materials are compared. It is shown here that the whiteness indices according to Berger for pyrogenic silicas and aerogels lie within specific ranges. Precipitated silicas, silica gels, and silicates show similar colorimetric results.

Properties, characteristics and conditions primarily associated with materials in general

colour reflectivity whiteness

dried or cured films

brightness

Miscellaneous terms

CIE system

Les mesures des caractéristiques réflectrices des produits de silice synthétique

Résumé

Des concepts tels que l'éclat ('brightness'), la valeur de référence de l'éclat A ('brightness reference value A') et l'indice de blancheur ('whiteness index') sont utilisés souvent dans un mauvais sens ou dans une façon qui donne naissance aux erreurs. Pour cette raison on propose des définitions de ces concepts importants. A base des mesures de grande envergure sur des produits de silice synthétique, on fait une comparaison des valeurs colorimétriques de divers groupes de matériaux. On démontre ici que les indices de blancheur Berger des silices pyrogéniques et des aérogels se trouvent entre les limites spécifiques. Les silices précipitées, les gels de silice et les silicates rendent les résultats colorimétriques semblables.

Reflektionsmessungen an synthetischen Kieselsäureproduckten

Zusammenfassung

Begriffe, wie, "Helligkeit", "Helligkeitsbezugswert A" und "Weissindex" werden häufig unrichtig oder in einer zu Irrtümern führenden Weise angewandt. Aus diesem Grunde werden diese wichtigen Begriffe definiert.

Gestützt auf zahlreiche, an synthetischen Kieselsäure-Produkten

Introduction

Refs. 1-10

For some time, a working group has endeavoured to establish a blackness index scale on a photometric basis for the colorimetric characterisation of pigment blacks^{1,2}. Now that the development work in this area has been almost completed³, interest has been focused on basic studies of silica products, because problems regarding them are gaining importance, and detailed results of reflection measurements on these materials have not, so far, been published.

In DIN 55 921 (Sheet 1) it is established that synthetic silicas and silicates for paints and other coating materials

vorgenommenen Messungen werden die kolorimetrischen Werte verschiedener Materialgruppen verglichen. Es wird hier gezeigt, dass die Weissindexe nach Berger für pyrogenische Kieselsäuren und Aerogele innerhalb spezifischer Werte liegen. Gefällte Kieselsäuren, Kieselsäuregele sowie Silikate ergeben gleichartige kolorimetrische Resultate.

must meet certain minimum requirements with respect to the brightness (brightness reference value A), namely:

synthetic silicas	>85,

synthetic silicates >93.

However, there are no documented results of research into the question of the extent to which colorimetric data can also serve for more accurate characterisation of such materials.

According to a new concept for DIN 55 921 dated October 1978, no further requirements as to brightness of synthetic silicas have been demanded. A comprehensive survey, in which whiteness index formulae and their practical significance for the paper industry are described in great detail, was presented by A. Berger⁴ in 1959. Similarly, various papers describe searches for a suitable whiteness index for application to textiles⁵⁻⁸. The fundamental principles of colorimetry and determination of whiteness indices were explained by B. Ziolkowsky⁹ in 1971.

As mentioned above, no studies of these synthetic silica products have been published in the past. The term "synthetic silica products" here includes pure silicas, as well as all technical products which are described as 'silicates', independent of their stoichiometry¹⁰.

In addition to the lack of information on the colorimetric characteristics of this group of materials, misunderstandings repeatedly arise in the description of various brightness levels and in quantitative data on the chromatic components, i.e., the components of a colour which determine its shade, because, in addition to concepts such as "brightness" and "brightness reference value A", other concepts exist such as "relative brightness" as well as a large number of whiteness indices, all of which represent a measure for how bright a filler, for example, appears to the human eye. What should be understood by these quantities, how they are calculated, and in what way they should be applied, will be explained in the first part of this paper. The second part gives the results of brightness and whiteness index measurements as well as a discussion of the results based on graphical comparisons. Finally, an explanation of the colorimetric expressions used in this work will serve to facilitate their employment.

Definition of basic concepts

Brightness and brightness reference value A

The definition of the brightness (and of the brightness reference value A) is to be found in DIN 5033, Part 1:

"The strength of a light sensation, as it is always inseparably associated with every colour sensation, is generally designated brightness. In the case of body colours, the brightness is an integral component of the colour. With body colours the brightness reference value A serves as a measure of the brightness. This brightness reference value is generally 100 times the luminous density factor β .

For body colours, in addition to the brightness reference made to the completely dead-white surface, it can also be useful to refer to the chromatically identical optimum colour, which contains the largest possible brightness reference value, A_0 , of the particular chromaticity.

The quotient

 $h = A/A_0$

is designated the relative brightness (according to Rösch)".

The standard specification for determining the brightness of filler and white pigment powders is contained in DIN 53 163, which also describes the way in which the moulded test specimen should be produced and what measurement conditions must be maintained.

In order to identify the brightness, the CIE-coordinate Y is used. Sometimes the so called "Y-reflection-index" (using the same abbreviation) is used. This index has ranges from 0 to 1 in contrast to the CIE-coordinate Y, which ranges from

0 to 100. This "Y-reflection-index" is identical to the radiant density factor, β , evaluated with the sensitivity $\overline{Y}(\lambda)$.

The Y-reflection-index is preferably determined for standard illuminant D 65 and the 10°-from-normal observer (D 65/10°), or alternatively, for standard illuminant C and the 2°-from-normal observer ($C/2^\circ$).

In contrast to the whiteness indices described below, the brightness reference value A represents an exactly defined measurement. This value is a pure bright-dark relationship and, therefore, does *not* take into consideration any chromatic components as do the various whiteness indices.

Whiteness indices

Ref. 11

In addition to the brightness and the brightness reference value A, various whiteness index formulae are of importance. One method for determining whiteness indices is given in ASTM E 313-73. The various whiteness indices serve, in the first place, to connect the physiological and psychic sensations within the eye with the physically determined brightness, and secondly, the whiteness index formulae also consider the more or less strongly chromatic component. The expression "whiteness index" itself does not represent a directly accessible measureable quantity, but instead it is a value which can be calculated on the basis of colour measurements and using various formulae depending on the area of application. These formulae differ from each other in that they favour to a greater or lesser degree certain hue components. About 20-30 whiteness index formulae exist¹¹. Therefore, it is reasonable to specify the whiteness index only when, at the same time, it is clearly understood which formula based on practical experience will be used in further work.

Some of the large number of whiteness index formulae which have been developed to date will be selected and described briefly below:

Whiteness index according to Hunter

$$W = L - 3b$$

In this evaluation, the brightness L = 10 enters into the formula as a square root function, and a bluish component of the test specimen increases the whiteness index.

Whiteness index according to Stensby

W = L - 3b + 3a

In this whiteness index evaluation, which is similar to Hunter's, the reddish components also contribute to higher values.

Whiteness index according to Berger

W = G + 3 B - 3 A

Using this equation, a blue-green preference with respect to the whiteness index is derived.

Other Whiteness indices

Additional whiteness index formulae have been developed by:

Taube	:	W = 4 B - 3 G
Ciba-Geigy	:	W = DY + Px + Qy + C
Stephansen	:	$W = 2 R_{430} - R_{670}$

1979 (4) REFLECTION MEASUREMENTS ON SYNTHETIC SILICA PRODUCTS

Harrison	:	$W = 100 - R_{670} + R_{430}$
Macadam	:	$W = (Y - k \cdot p_c^2)^{\frac{1}{2}}$
Judd	:	$W = (Y - K \cdot S^2)^{\frac{1}{2}}$

Studies of synthetic silica products

Measurement results

Since no results of studies made of synthetic silica products have yet been published, measurements were made on a large number of synthetic silicas, silicates, silica gels, and aerogels in the form of molded-powder test specimens. In all, these measurements were made on

20 pyrogenic silicas	from 4 manufacturers,
35 precipitated silicas	from 7 manufacturers,
13 silica gels	from 4 manufacturers,
5 aerogels	from 2 manufacturers, and
13 silicates	from 5 manufacturers.

The measurements were made using an automatically operating multifilter spectrophotometer (24 filters) RFC 3 manufactured by C. Zeiss, Oberkochen.

Table 1 gives a comparison of the brightness reference values A, the brightness values according to Hunter, as well as the whiteness indices according to Stensby and Berger.

Table 1

Ranges of the brightness reference value A, the brightness according to Hunter, as well as the whiteness indices according to Stensby and Berger for various groups of synthetic silica products

Product Group	Brightness Reference Value A	Brightness (Hunter)	Whiteness Index (Stensby)	Whiteness Index (Berger)
Pyrogenic silica	84 - 98	91 - 100	96 - 101	97 - 108
Precipitated silica	86 - 97	93 - 99	90 - 97	85 - 96
Silicates	93 - 98	96 - 99	93 - 97	88 - 95
Silica gels	90 - 97	95 - 99	91 - 97	85 - 96
Aerogels	87 – 94	93 - 97	88 - 90	78 - 82

The test specimens were prepared according to the specification given in DIN 53 163, and the measurements were made using the RFC. The evaluation was made for standard illuminant C and 2°-from-normal observer ($C/2^\circ$).

Discussion of the results

Ref. 12

In order to evaluate the results, an attempt was made to clarify the colorimetric relationships by means of various graphical representations. In Figures 1–3, the ranges are plotted within which results were found for the individual classes of materials.

In contrast, Figures 4–7 show the spectral distribution of the reflection index of the examples selected. Whilst Figs. 4 and 7 reproduce the results found on pure silica products, i.e., silica products not subjected to any aftertreatment, Figs. 5 and 6 show the reflection curves plotted with surfacemodified silicas.

Brightness reference value A and whiteness indices

It can be seen from the diagram shown by Fig. 1, in which the brightness reference value A was selected as the independent parameter, that:

The widest range of dispersion is shown by the pyrogenic silicas, whilst the dispersion range of the silicates is relatively narrow.



Fig. 1. Ranges of the brightness value A for various silica products

All silicates studied meet the conditions specified by DIN 55 921, according to which the value 93 is allowed as the lower limit.

The synthetic silicas also show brightness reference values considerably higher than 85.

The brightness reference value A is not suitable for characterising various silica products because all ranges overlap.

In Fig. 2 the whiteness index according to Berger is plotted. The advantages of this type of representation are obvious because a division of the individual ranges can be recognised immediately.



Fig. 2. Whiteness index according to Berger as an aid to characterise synthetic silica products

The following conclusions can be drawn from this graph:

The pyrogenic silicas have the highest values (>95), and the aerogels have the lowest values (<83).

The precipitated silicas, silicates, and silica gels lie between these materials.

A characterisation using the whiteness index according to Berger is, therefore, clearly possible for pyrogenic silicas and aerogels.

The precipitated silicas, silica gels, and silicates can not be differentiated.

In Fig. 3 an attempt is made to find a relationship between the whiteness index according to Berger and the BET surface area with the pyrogenic silicas. Observing the necessary caution, some correlation can be recognised. Because in Fig. 3 the whiteness index also appears to assume higher values proportional to the BET surface area, at least up to 300 m²/g, the subsequent decrease can possibly be attributed to a certain porosity in the very finely divided silicas.



Fig. 3. Whiteness index of pyrogenic silicas according to Berger in various BET surface area ranges

Spectral variation in reflection

Fig. 4 shows the principal optical differences between a pyrogenic silica (*Aerosil*) and an aerogel (*Santocel C*). Whilst *Aerosil* is a substance with a bluish tinge, *Santocel C* has the highest reflection values in the red wavelength region. This is typical for both classes of materials. Although *Syloid 244* has recently been included in the literature with the aerogels, because of its modification in production and its characteristics¹², in terms of its spectral reflection dependence, it clearly reacts like a silica gel or a precipitated silica (see Fig. 7).



Fig. 4. Reflection of two silica aerogels and one silica aerosol (pyrogenic silica)

The possibility of influencing synthetic silica products in their behaviour on application exists by coating the silica surface with wax.

Many different grades of waxes in varying amounts are used.

Fig. 5 shows the reflection of such silica products from different manufacturers; it can be seen that:

Coated products possess about the same brightness as the untreated grades (level of the reflection curve) (see also Fig. 7),



No correlation exists as to C-content and with this to the amount of wax,

Apparently the kind of wax is dominant, since with almost equal C-content the character of the reflection curve can show clear differences.

The different reflection characteristics of coated silicas are of some significance for analytic considerations but not, however, in their applications.

Chemically modified silicas are obtained, for example, by causing the silanol groups to react, usually with suitable organosilane compounds. As a result of this reaction, the silicas largely lose their hydrophilic characteristics. A study was made to determine whether the spectral reflection distribution changes characteristically with this surface modification. Fig. 6 shows that only gradual differences can be recognised in comparison with the corresponding untreated products which are represented in Fig. 7.



Fig. 6. Reflection of chemically converted silicas (precipitated silicas Sipernat D17 and D15, and pyrogenic silica Aerosil R972)



Fig. 7. Reflection of four representatives of different silica products

The following points are noteworthy in Fig. 7:

All curves show a similar variation, even though a synthetic, amorphous silicate (aluminium silicate P 820), a precipitated synthetic silica (Sipernat 22), a synthetic amorphous silica gel (Syloid 621), and an amorphous silica produced by the arc process (flatting agent TK 900) are compared with each other.

Distinguishing features appear more in the brightness.

The thermally produced TK 900 does not have higher reflection components in the blue range, a characteristic of silicas derived in the oxyhydrogen flame (Aerosil).

Reproducibility of the measurements

In order to check the range of error of a single measurement, Table 2 gives the results of measurements made on 10 specimens molded from the same test material.

Table 2 Ten measurements made on Aerosil 200, average values and standard deviations (test specimens newly moulded for each measurement)

Aerosil 200	CI	CIE coordinates			Whitene	ss index
	X	Y	Z	(Hunter)	(Stensby)	(berger)
1.	87.01	89.14	109.42	94.41	99.6	103.5
2.	85.34	87.41	107.61	93.49	99.3	102.4
3.	84.15	89.32	109.93	94.51	100.0	104.7
4.	88.40	90.50	110.04	95.13	78.8	101.5
5.	86.36	88.48	108.68	94.06	99.3	102.9
6.	87.84	89.95	109.70	94.84	99.0	102.0
7.	88.23	90.35	110.08	95.05	99.0	102.1
8.	87.69	89.82	109.66	94.77	99.0	102.3
9.	86.81	88.99	109.62	94.33	99.9	104.7
10.	89.12	91.23	110.60	95.51	98.6	101.2
Average		89.52±1.10		99.3±0.5		
values and standard deviations				94.61±0	.58 10	02.3±1.2

Since it is not clear from the values in Table 2 whether the relatively large standard deviations result from inaccuracies in measurement, 10 measurements were also made on the same test specimen (another specimen).

Table 3 shows the results of these measurements.

A comparison between the standard deviations given in Tables 2 and 3 shows that the inaccuracies of repetitive measurements must be attributed to uncertainties in the production of the test specimens. Differences in the compression probably have an especially significant effect on the reflection values.

Production of the molded test specimens with a manuallyoperated press, as specified in DIN 53 163, is affected by too many subjective factors. A more clearly defined method of producing the test specimens must, therefore, be developed for studies with small measurement differences.

Received 7 December 1978

Table of colorimetric expressions used

Syn	nbol	Represents
<i>X</i> ,	Y, Z	CIE coordinates (DIN 5033, sheet 2)
x, y	', z	Chromaticity coordinates $\left(\text{for ex. } x = \frac{X}{X+Y+Z} \right)$
A	=	Y brightness reference value (DIN 5033, sheet 1)
h	-	A/A_o Relative brightness (DIN 5033, sheet 1)
β(n)	=	Radiant density factor or luminous density factor (DIN 5036, part 1)
λ	=	Wavelength of the light
D 6	5, C	Standard illuminants (DIN 5033, sheet 7)
L a b	=	$ \begin{array}{c} 10\sqrt{Y} \\ 17.5 \cdot (1.0524 \cdot X - Y)/\sqrt{Y} \\ 70 \cdot (Y - 0.91891 \ Z)/\sqrt{Y} \end{array} \end{array} \right\} \begin{array}{c} \text{acc. to Hunter} \\ \text{(ASTM D 1365 - 60 T)} \end{array} $
W	=	Whiteness index
G	=	Y Correspond approximately to the
A	=	1.299 $X = 0.215 Z$ components of the green, red,
B	=	0.9189 Z \int according to Berger and Taube
R	=	Reflection index at certain wavelength

(The constants D, P, Q, C, as well as k, Pc, Ks, and S are explained in the literature references listed.)

Test specimen	X	Ŷ	z	L	Whiteness index		
					Berger	Stensby	
1. Measurement	86.56	88.37	100.89	94.00	77.3	86.6	
2. Measurement	86.55	88.35	100.90	93.99	77.4	86.7	
3. Measurement	86.56	88.36	100.92	94.00	77.4	86.6	
4. Measurement	86.56	88.35	100.93	93.99	77.5	86.8	
5. Measurement	86.55	88.34	100.90	93.99	77.4	86.8	
6. Measurement	86.53	88.33	100.83	93.98	77.2	86.6	
7. Measurement	86.53	88.33	100.85	93.98	77.3	86.6	
8. Measurement	86.51	88.31	100.86	93.97	77.4	86.7	
9. Measurement	86.57	88.38	100.91	94.01	77.4	86.7	
10. Measurement	86.58	88.37	100.95	94.00	77.5	86.8	
Average value Standard deviation		88.35 0.022		93.99 0.012	77.4 0.092	86.7 0.088	

Table 3
Ten measurements made on the same test specimen, average values and standard deviations

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Avoiding paint failures by prohesion*

By F. D. Timmins

Consultant, Mebon Ltd, Huthwaite, and Mond Division ICI Ltd, Wythenshawe

Summary

Prohesion describes a simple philosophy, namely that "Protection is adhesion". The paper reviews the extensive experience of a major industry which has pioneered the use of modern methods of application and high build protective systems.

A test procedure is described which incorporates unavoidable application malpractices, modifies established accelerated tests

Keywords

Types and classes of coatings and allied products

primer

Types and classes of structures or structures or surfaces to be coated

steel

Raw materials for coatings binders (resins, etc.)

> alkyd resin chlorinated rubber styrene alkyd resin

chemically active pigments

zinc chromate zinc phosphate barium metaborate to correlate with practice and predicts ageing characteristics of modern paint systems.

Failures encountered in practice have been critically investigated and a new concept in primer adhesion failure is presented, together with unorthodox modifications in formulation.

Process and methods primarily associated with analysis, measurement or testing

> salt spray testing impact testing

surface preparation before coating

grit blasting

Properties, characteristics and conditions primarily associated with dried or cured films

durability weather resistance

reather resistance

Specifications, standards and regulations

test specification

Comment éviter les défauts de peintures par prohesion

Résumé

Par le mot *prohésion* on décrit une philosophie simple, à savoir "la Protection c'est l'adhérence".

L'exposé passe en revue l'expérience considérable d'une industrie importante qui est un des pionniers de l'emploi des méthodes modernes d'application et des systèmes protecteurs "high-build".

On décrit un procédé d'essai, qui renferme les méfaits inévitables à l'égard de la technique d'application, en vue de modifier les

Vermeidung von Anstrichschäden durch Prohesion

Zusammenfassung

Prohesion bezeichnet eine einfache Philosophie, nämlich dass "Schutz ist Haftung". Die Arbeit betrachtet die weite Erfahrung einer Grossindustrie, welche moderne Anwendungsmethoden sowie Dickschichtschutzsysteme pionierte.

Ein Prüfverfahren wird beschrieben, das unvermeidliche Falschanwendungen einschliesst, eingefährte Kurzprüfungen modifiziert

Introduction

Chemically resistant paint systems capable of withstanding severe climatic conditions are well established. Their durability is essentially dependent on the adhesion of the primer to the substrate and behaviour at damaged areas, sharp edges, etc.

*Lecture presented to the Bristol Section on 30 March 1979

essais de vieillissement accélérés traditionnels afin de les mettre en corrélation avec la pratique, et qui prédit les caractéristiques de vieillissement des systèmes modernes de peintures.

On a fait une investigation critique des défaits rencontrés dans la pratique, et l'on présente à la fois un nouveau concept de la perte d'adhérence des peintures primaires, et des modifications exceptionnelles de la mise au point des formules.

zweks Korrelation mit der Praxis und Alterungscharakteristika moderner Anstrichsysteme voraussagt.

Bei der Verarbeitung vorkommende Anstrichschäden wurden kritisch untersucht, und es wird eine neue Vorstellung für Primer-Haftungsfehler vorgeschlagen und gleichzeitig eine unorthodoxe Modifizierung der Rezeptierung.

Laboratory tests, such as sulfur dioxide and sodium chloride environments, continue to influence development, although they bear little or no resemblance to natural conditions.

Furthermore, they rarely predict typical failures due to application malpractices or undue physical change.

This paper describes a logical approach to the problem of predicting long life protection in the order of 20 years or more. It represents an intensive investigation carried out in a laboratory which, over a period of 50 years, has established an international reputation as a realistic user, specifier and test authority.

No relevant aspect was overlooked. Test methods were significantly revised to correlate with natural exposure and to take account of application malpractices.

The success of the modified salt spray test enabled fundamental changes to be made in pigment performance and finally a simple test was developed to predict undesirable physical/chemical changes due to ageing.

The combined test procedure reflects a 'priority' philosophy which cannot fail to eliminate inadequate or incompatible paints. It is described as 'Prohesion' which simply means protection by adhesion and implies that adhesion failure precedes corrosion, not vice-versa.

Test methods

Effect of substrate profile

Blast cleaning operations in the UK employ a wide variety of abrasives. Profile amplitudes averaging 100 microns are normally acceptable and providing the standard of cleanliness falls within SA21-SA3, little or no attention need be paid to rogue peaks.

A major primer investigation carried out in the British Rail laboratories was rendered ineffective owing to the influence of random rogue peaks. The test specimens had been automatically blasted using G.24 abrasive (works



Fig. 1. Influence of adhesion on corrosion at cross hatchings after 500 hours BR 77 accelerated test.

Left: smooth steel (Pyrene Ltd) Right: grit blasted steel Top process: Expoxy polyamide/zinc phosphate primer (25 microns) Chlorinated rubber (50 microns)

Bottom process: Expoxy polymide/zinc rich primer (25 microns) Chlorinated rubber (50 microns) production). During about the same period, an investigation into a premature failure on a prestige structure clearly indicated the cause to be due to rogue peaks.

Reversion to smooth steel panels was rejected since previous tests had shown that the two most extensively used blast primers in Britain did not adhere to smooth surfaces. Since the removal of rogue peaks is generally unacceptable on economic grounds, it was decided to standardise on a profile produced by coarse grit and so build into the test a 'real life' malpractice. The abrasive selected was 'J' Blast Grade B, a non-metallic abrasive supplied by Hodge Clemco. This abrasive produces a uniform distribution of rogue peaks of amplitudes up to 200 microns.

Primers were applied to the 'J' Blast specimens at a dry film thickness of 25 microns and subjected within 4 hours to the newly developed BR 77 salt spray test. Primers lacking true inhibitive pigments failed within 12-48 hours, showing extensive peak corrosion. The severity of the test simulates adverse conditions often experienced during site application and in the case of new steelwork, and covers the delay period between shop priming at the steel mill and overcoating at the fabricator's works.

Nevertheless, certain combinations of pigments provided outstanding protection and since the test is specific and quick, it offered an opportunity to review the pigment's contribution to the primer efficiency. It is worthwhile noting that an academic test carried out using the same primers applied to smooth steel failed to detect major differences over a period of 200 hours.

The primer medium employed was chlorinated rubber/ alkyd. Wash primers, owing to their low film build (8-10 microns), exhibited severe peak corrosion within 12 hours and zinc rich (organic and inorganic) primers developed extensive white corrosion products.

Primers failing the new BR salt spray at the 48 hour stage were eliminated. Those considered satisfactory were applied to specimens blasted with G.24 steel grit which had been scraped to remove rogue peaks. After overcoating with the full system, the specimens were subjected to long duration weathering, new BR 77 salt spray and ageing/impact tests.

BR 77 salt spray test

Refs. 1, 2

British Rail were the first test authority to specify a sulfur dioxide/humidity test (1935). Although extensively used in addition to BSS Salt Spray 3900, the results obtained have been viewed with reservations, as opposed to the more reliable natural weathering and field tests.

An alarming discrepancy between natural weathering and accelerated tests on high build coatings motivated a significant modification to the salt spray test, namely:

The enclosed cabinet was replaced by a BS weatherometer, its UV lamp being substituted by a salt fog spray. Since the test specimens are located on the side of the revolving drum, they are subjected to a uniform test atmosphere, in direct contrast to the random location of test specimens in cabinets.

The normal 5 per cent salt solution was replaced by a weak solution of Dr J. B. Harrison's mixture^{1,2} viz 0.40 per cent ammonium sulfate and 0.05 per cent sodium chloride.

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The continuous saturated atmosphere of the BSS salt spray was replaced by cycling over 24 hours, 6×3 hour periods of salt spray alternating with 6×1 hour drying periods using ambient air.



Fig. 2. BR 77 salt spray apparatus

Comparing the results obtained in the BR 77 salt spray with natural exposures accumulated over 10 years showed that a significant advance in correlation had been achieved.

In particular, adhesion failure (undercut corrosion) from cross hatch and edges was convincingly realistic.

Cycling, air enrichment and significant reduction in salt contaminant, in addition to ambient temperature, must obviously relate more closely to natural environments than the artificial, passivating, elevated temperature conditions encountered in most conventional salt spray tests.

The mechanism of paint breakdown is essentially due to loss of film integrity due to the movement of water (vapour) in and out, arising from wetting and drying periods.

Pigment in primers

The Health and Safety legislation necessitated a review of all available lead free inhibitive pigments which was completed using the BR 77 salt spray test.

The pigments were incorporated according to manufacturers' data sheets into a chlorinated rubber/alkyd medium (PVC 35.0 per cent). The primers were applied (film thickness 24-30 microns) to 'J' Blast 'B' treated panel.

The severity of the test readily indicated the capability of the pigment in restraining corrosion at weak rogue peak areas. Inert pigments such as zinc phosphate and Nalzin were totally ineffective, whereas zinc chromate was somewhat better. A combination of 20.0 per cent zinc phosphate and 5.0 per cent zinc chromate was outstanding. A subsequent investigation indicated that barium metaborate may replace zinc chromate.

Whilst the performance of the zinc phosphate/zinc chromate combination had established the principle of a solublt active suppressant and a film integrity pigment, it should not be overlooked that different media may require significanc modification of the pigmentation. Thus, it is established that zinc phosphate contributes nothing to a styrene acrylie aqueous medium, whereas zinc chromate itself is remarkably effective. Furthermore, a double coating reduced the sensitivity of the rogue peak areas and smooth steel panels failed to simulate early corrosion failures, but subsequently revealed loss of film integrity, in formulations lacking a barrier pigment.

The severity of the test is justified, since it is quite common in practice to find primers are thinned or applied thinly in the interests of saving money.

Finally, a simple check test was devised to classify inhibitive pigments without needing to prepare a paint.

A new bright neil was cleansed with boiling deionised water and placed in an airtight bottle containing 100 ml of 0.1 per cent Dr Harrison's mixture and 1.0 gram of the pigment under test.

Two classes of results were obtained according to freedom of rusting:

Those containing soluble active electrochemical corrosion suppressant, viz. zinc chromate, barium metaborate;

Inert pigment which offered no resistance to copious rusting, *viz*. zinc phosphate, Nalzin, calcium ferrite, zinc ferrite.

Note

- (1) 20.0 per cent zinc phosphate/5.0 per cent zinc chromate on the paint.
- (2) Dr Harrison's mixture:

3.25 per cent ammonium sulfate

0.25 per cent NaCl.

Behaviour of primer at cross hatchings

Adhesion failure (undercut corrosion) at cross hatch areas produced by standard weatherometer, salt spray and sulfur dioxide tests may bear little resemblance to those which develop after several years of natural exposure.

British Rail were the first test authority to specify the use of zinc phosphate (1970) although it had been developed by Dr J. B. Harrison many years previously.

This pigment faciliated the complete elimination of lead pigments, introduction of airless spray technique, rheological control and formulation stability.

Accelerated weathering tests predicted good durability. In addition, natural exposure tests on primers were encouraging.

Unfortunately, after 3-5 years natural exposure, alarming adhesion/corrosion failures developed at cross hatch areas and edges on a variety of high build systems, such as, epoxy polyamide, modified pitches, chlorinated rubber etc.

The worst failure occurred with zinc phosphate pigmented epoxy polyamide blast primers, whereas zinc rich epoxy polyamide primer was far superior and zinc tetroxy chromate polyvinyl butyral primer, even better.



Fig. 3 Extensive adhesion failure due to a top impermeable primer after 7 years exterior exposure using grit blasted steel

Process: Expoxy polyamide/zinc phosphate primer (25 microns) Epoxy polyamide/micaceous iron oxide undercoat (40 microns)

Epoxy polyamide/micaceous iron oxide finish (40 microns) Chlorinated rubber coating applied after 3 years exposure (2 microns)

A general review of long term natural exposure tests indicated that extensive adhesion/corrosion failures were accelerated by:

- (a) Smooth steel surfaces;
- (b) Only inert pigment in primer;
- (c) Impermeable primer media;
- (d) Excessive total film thickness.

The most outstanding performance was shown by a three coat styrene acrylic dispersion system applied to a SA.2 blasted piece of rusted wagon plate. The primer pigmentation was red oxide/zinc chromate. The total film thickness was 150 microns and after 14 years, no failure of any description was detected. It is worthwhile recording that the three coats were applied at hourly intervals outside, under cover, on a wet, humid (95 per cent RH) day.

The BR 77 salt spray realistically confirmed the natural exposure observations. Significant reduction in cross hatch adhesion/corrosion failure was obtained by introducing 5.0 per cent zinc chromate into:

- (a) Zinc phosphate epoxy polyamide blast primer;
- (b) Metallic zinc epoxy polyamide blast primer;
- (c) Epoxy powder coating.

Processes applied to smooth steel failed rapidly and several proprietary polyvinyl butyral based blast primers were excellent.

The investigation indicated that a minor degree of water sensitivity in both primer medium and pigment substantially improves adhesion at damaged areas in the paint system. It would appear that unless moisture can enter the primer film, it will probe underneath, thus resulting in adhesion failure.



Fig. 4. Influence of primer permeability on adhesion at cross hatchings after 6 years exterior exposure on smooth steel (Pyrene Ltd) *Left:* Polyvinyl butyral/zinc chromate primer (10 microns) *Right:* Epoxy polyamide/zinc phosphate primer (30 microns) *Top coats:* Vinyl toluenated alkyd undercoat (25 microns) and vinyl toluenated alkyd finishing coat (25 microns)

Reduction of long-life durability

BR 77 salt spray provides a realistic means of formulating and testing processes capable of adhesion and protecting at the primer stage under adverse conditions and retaining adhesion at damaged areas in the full system. It cannot, however, predict future incompatibility arising from physical/ chemical changes due to ageing.

In an era of long-life protection, ie 20 years or more, it was imperative to establish a reliable method of test.

A fundamental weakness of all paint media, namely the increase in embrittlement at low temperature, was selected by British Rail as a means of fingerprinting relative physical/ chemical changes due to ageing.



Fig. 5. Influence of temperature on adhesion after impact (BR "POP" test)

Extreme left		Extreme right
-5°C	>	20 C
Intercoat failure		Satisfactory

Ageing involves complete elimination of solvent, oxidation, cross linking etc. and it was considered that 30 days' contioning in an oven at 40°C is adequate.

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Fig. 6. BS 3900 Part E.3. Impact test

The full system is applied in accordance with the manufacture's instructions to a $SA2\frac{1}{2}$ -SA3 steel panel blasted with G.24 grit and scraped to remove rogue peaks.

After heat conditioning, the test panel is placed in a refrigerator at -5° C for 24 hours. It is then removed and immediately subjected to BS3900 Part E.3 impact test. Scraping the indent with a knife instantly reveals substrate or intercoat adhesion failure.

The test is extremely severe, but it does represent a practical hazard and it can be made more selectively by impacting the specimen at intervals, until it reaches ambient temperature.

Impact can also be carried out on an unconditioned specimen and any specimen which has been subjected to other accelerated weathering tests.

This test described as BR, POP Test (Prediction of Performance) conclusively eliminates processes which are inherently incompatible. It is not unreasonable to assume that a process which satisfies the test is virtually incapable of exhibiting serious adhesion failures even over a life of 20 years or more.

It is also reasonable to assume that such a process which does develop adhesion failures in practice has not been applied in accordance with the paint manufacturers' recommendations.

Acknowledgments

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Accelerated weathering tests*

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Summary

An attempt to compare various accelerated weathering devices with respect to the correlation of the results obtained from short term tests with those from natural long term exposure and in practice. The respective merits of laboratory test cycles and ac-

Keywords

Processes and methods primarily associated with analysis, measurement or testing

accelerated weathering test procedure weatherometer

manufacturing or synthesis

gloss retention

Les essais de vieillissement accélérés

Résumé

On a essayé de faire une comparaison de divers appareils de vieillissement accéléré en vue d'établir une corrélation entre les résultats rendus par les essais de courte durée et ceux rendus par l'exposition aux intempéries à longue durée et dans la pratique. On discute les avantages respectifs des cycles employés dans les

Kurzbewitterungsprüfungen

Zusammenfassung:

Ein Vergleich verschiedener Kurzbewitterungsgeräte im Hinblick auf die Korrelation zwischen den Ergebnissen von Kurzprüfungen und solchen von langfristigen Prüfungen und der Praxis. Bewertung der Prüfungsmethoden im Laboratorium und der Beschleunigung

Introduction

Ref. 1

This subject, undoubtedly the most controversial in the study of surface coatings, may be introduced by quoting the closing sentences of a review on weathering tests compiled about two years ago¹:

"Progress in all the fields involved enhances the possibility of relating weathering results to actual service conditions. Some lack of agreement, however, is bound to persist, owing to another natural factor—as complex as the weather—the individual approach to weathering tests."

These words summed up the author's personal view which as a conscientious reviewer she tried to conceal. It is not intended to do so here.

The objectives of testing will be discussed and the various types of accelerated weathering test devices considered. Results obtained from an exposure series will be given to illustrate how far correlation of results can be achieved. Finally, a few interesting views published by international experts during recent months will be quoted. celeration of the effect of solar radiation, the natural light source, are discussed.

Views from certain recent papers are quoted, which appear to confirm some of the experimental findings.

Properties, characteristics and conditions primarily associated with dried or cured films

chalking weather resistance

essais au laboratoire, de l'accélération de l'effet de la radiation solaire, la source naturelle de lumière.

Les points de vue de certains auteurs qui semblent à donner confirmation des résultats expérimentaux sont cités.

des Einflusses der Sonnenstrahlung, der natürlichen Lichtquelle.

Zitate aus einigen, in jüngster Zeit erschienenen Artikel, welche die Versuchsergebnisse bekräftigen zu scheinen.

Objectives

Refs. 2-6

The objectives of accelerated testing will vary according to the person or organisation interested in the results. They may be for example:

(1) Users of paints.

(2) Manufacturers of testing devices, designers and/or operators of accelerated test methods.

(3) Independent test services.

(4) Producers of coating materials.

The most exacting user of surface coatings is the motor industry. Car manufacturers issue strict specifications covering composition, application properties and durability requirements of the products supplied to them.

One year's exposure in South Florida, without substantial deterioration in appearance, represents one of the old established standard requirements.

F When durability testing on sites in South Florida was introduced around 1930, the two to three fold acceleration

*Lecture presented to the Thames Valley Section on 7 December 1978.

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in the weathering rate of finishes in that subtropical region as compared to those in temperate climates resulted in a very rapid failure of the materials in use at that time. Hence, Florida exposure was taken as an accelerated outdoor weathering test. For today's high quality surface coatings, direct natural exposure in Miami is regarded as "real time" exposure, against which the results obtained with various accelerated weathering devices may be compared.

Certain industrial paint users specify exposure for 1000 hours in a weatherometer, and several motor manufacturers use indirect outdoor exposure in Arizona on *Emmaqua* machines for 160,000 Langleys ($1 \text{ ly} = 1 \text{ g cal}(\text{cm}^2)$. This amount of irradiation is obtained in about 5 weeks and furnishes results comparable to those of 6 months direct exposure in South Florida.

Manufacturers of equipment, designers of test methods and scientists involved in testing, have contributed an immense amount of effort to the development of reliable testing methods. Working in close co-operation with the chemists and technologists involved in the manufacture of the products to be tested, and studying the theoretical background of weathering phenomena, they have published many papers. This vast literature provides most of the present knowledge on the principles of durability testing. The purpose of this continuous research on their part is intended to perfect the apparatus, in order to obtain reproducible results within the minimum feasible time and having a good correlation with results found after long term natural exposure in practice.

Amongst the various types of accelerated laboratory weathering equipment available, the Marr Artificial Weathering apparatus (UK) (BS 3900/F3), the Atlas W types (USA) (ASTM 02565) and the Hanau Xenotest 1200 (WG) are most widely used. The QUV Cyclic UV Weathering Tester (USA) has been introduced more recently. The procedures to be used are all covered by National Specifications and international standardisation is in the course of preparation by the ISO Technical Committee 35.

Independent test services usually operate in areas where the existing natural weather conditions already enhance the breakdown of organic coatings, eg the high solar radiation coupled with high humidity in South Florida, and the even stronger solar radiation with a very high proportion of UV in the Sonora Desert of Arizona, although with a rather low humidity.

Some acceleration of the weathering effect of direct natural exposure can be achieved by varying the angle at which the sample is mounted or by increasing the heat effect, for example, by the so-called "black box" (simulating more closely the practical conditions occurring on motorcars), but such modifications reduce the required exposure time only slightly.

A real breakthrough was achieved in 1960, with the introdustion of indirect solar irradiation by means of the *Emma*^{*} and *Emmaqua*^{*} machines² in Phoenix, Arizona. Caryl and Helmick's development of the automatic equatorial mount into an accelerated outdoor weathering device^{3,4} brought outdoor testing times within the time limits for artificial weathering in the laboratory, whilst retaining the undisputed advantage of using the sun as the light source. These machines, solely operated by DSET Laboratories Inc.⁵, have the samples mounted on the underside of a cross-member at the top of the machine, and 10 highly polished special aluminium mirrors are positioned so as to reflect the sun's rays (which strike them at an angle of about 90°) on to the target area above. Both types can be operated only during daylight hours, ie 8–9 hours according to the season of the year. Whilst *Emma* is designated to simulate more arid conditions, the *Emmaqua*, on which the samples are automatically sprayed with demineralised water for 8 minutes during each hour of operation, corresponds to wetter climates.

Because of their natural light source, such devices can function with efficiency only under the climatic conditions for which they were originally designed. About 250 of these machines are now in constant use at the New River site, weathering samples of world-wide origin.

The objectives of independent commercial test services are similar to those of the producers of testing apparatus, but with the added responsibility of performing tests for their clients. In addition to continuous improvement of testing facilities, they are also involved in the constant observation and recording of climatic variations (eg measurement of incoming solar radiation at various angles, and measurement of direct sunshine only, recording of total UV radiation less than 383nm, wind velocity, temperature, humidity, etc.) to enable a realistic evaluation of the accelerated results obtained⁶.

Producers of coating materials have different objectives. Accelerated testing, as specified by their customers in the automotive and industrial finishing field, is only one of them.

In development and research work time is a dominant factor. Accelerated weathering has to be relied upon to enable improvements in formulation during development and to avoid discovering some failure when it is too late.

New products must be tested and retested long before reaching the market, and even before their presentation to the higher authorities within the organisation. It is at this early stage where accelerated test methods have to be carefully selected, according to the nature of the project.

Ideally, questions of economics should not enter into a technical discussion, but they cannot be avoided. Accelerated weathering tests are far more expensive than long term natural exposure performed, often with some lack of efficiency, on the roof-top of a paint factory.

If tests are carried out in the paint laboratories, accelerated weathering tests involve the purchase of the apparatus, which is rather expensive. Thereafter, running and maintenance costs are involved, such as replacement of light sources, cost of electrical power, deionised water, etc. Furthermore, at least half a year of expert staff's time is needed to develop the suitable exposure period in terms of light and wetting cycles, which are designed to produce accelerated results that bear some correlation to reality. The best of laboratory equipment is worthless if it is not properly operated.

On the other hand, at first sight, the fees charged by the independent testing organisations for the accelerated weathering of samples might seem high, but what do they offer in return? Objectivity, up-to-date apparatus, operated and maintained by well trained staff with great expertise in the testing procedure. It is true that some delay is caused by

^{*}Emma = Equatorial Mount with Mirrors for Acceleration Emmagua = Emma plus water spray

transporting samples to test sites overseas, but air-mail does not take long and this time lag is offset by avoiding the usage of manpower, time and saving costs of performing the accelerated tests within the company's own research and development laboratories.

Experimental,

Refs. 7, 8

Almost ten years ago a graph (see Figure 1) illustrating the course of gloss deterioration of identical finishing systems exposed under natural conditions in Florida and natural as well as accelerated conditions in Arizona suggested, that except for the speed of deterioration, the actual nature of the ageing process remained the same on both sites under identical conditions of exposure, and hardly varies if exposure is under the accelerated outdoor conditions on *Emmagua*⁷.



Fig. 1. Deterioration of gloss on accelerated and natural outdoor exposure

This finding seemed worthy of investigation and led to further test series, performed between 1971 and 1975, reported in a paper presented in 1976 at the FSCT meeting in Washington⁸.

The present experiment is a follow-up to the previous ones, again with industrial development work in mind. The scope remained the same, namely an attempt to correlate the results obtained in short- and long-term weathering tests. However, the emphasis was shifted from the coating systems under test to the comparison of the available weathering procedures.

Coating systems tested

Two white motor finishes were chosen, an acrylic and an alkyd based type. Both had been continuously produced on a works' scale for a long time with only minor modifications

which normally occur over the years. Both were tested in earlier experiments, providing the chance for checking on the repeatability of the different weathering tests.

Weathering tests performed -

- (1) Miami, 5° South, Summer 1977-Spring 1978, 9 months
- (2) Phoenix *Emmaqua* September—October 1978, 240,000 Langleys (=about 8 weeks)
- (3) Marr Weatherometer BS Cycle 1000 hours
- (4) QUV Tester, Cycle: 8h UV 60–65°C 16h Humidity 50–52°C 240 hours

Data recorded

60° Gloss readings at specified periods

Colour difference ΔE (only after accelerated *Emmaqua* exposure). Chalking, visual observation only.

Results of this experimental series appear in Tables 1, 2, 3 and 4 and Figures 2 and 3.

 Table 1

 White motorcar finishes, samples and initial gloss values

Panel No.	Туре	60° Gloss%	
5	Low stoving acrylic	91	
6	Thermo-setting alkyd	90	

Table 2 Percentage gloss retention* on accelerated outdoor exposure Phoenix, September—October 1978 (Emmaqua)

Langleys received:									
80,000 lys.	160,000 lys.	240,000 lys.							
92	82	69							
95	87	64							
	Langley 80,000 lys. 92 95	Langleys received: 80,000 lys. 160,000 lys. 92 82 95 87							

Table 3 Percentage gloss retention* on natural outdoor exposure Miami, July 1977—March 1978 (5°South)

		Time:		
Pane	el No.	3 Months	6 Months	9 Months
×	5	75	56	49
	6	79	66	61

*Note: Gloss retention is expressed in percentage of the initial gloss value.

Table 4

Percentage gloss retention on accelerated laboratory exposure

	QU	V Apparatus	Marr Weatherometer			
Panel No.	240 hrs	Note	1000 hrs	Note		
5A*	84	Slight loss of gloss	99	No visible change		
5B*	93	No visible change				
6A	44	Strong chalking	95	No visible change		
6B	45	Strong chalking				

*A and B mean repeated tests.







Fig. 3. Percentage gloss retention on natural outdoor exposure. Miami, July 1977 to March 1978. 5°South

Tables 5a, 5b, 6a and 6b and Figures 4, 5, 6 and 7 demonstrate the repeatability of natural exposure tests in Miami at 5°South and accelerated outdoor tests in Phoenix on *Emmaqua* in different years and seasons of the year.

	Table 5A
Repea	tability of accelerated outdoor exposure tests
on	acrylic finishes (Phoenix : Emmaaua)

	Data	Langleys received*							
Panel No.	Year and season	80,000 lys.	160,000 lys.	240,000 lys.					
49	1971-72 Winter	96	84	60					
53	1975 Spring	97	89	49					
5	1978 Autumn	92	82	69					

*The irradiation of 240,000 Langleys (I y=1g cal/sq cm/min) is achieved within 45-60 days depending on the seasonal weather variations.

Table 5B	
Repeatability of natural outdoor	exposure tests
on acrylic finishes (Miami	: 5°South)

	Data	Time: Months						
Panel No.	Year and Season	3 Months	6 Months	9 Months				
49	Dec. 1971-Sept. 72	86	74	56				
53	Dec. 1974-Sept. 75	84	80	67				
5	Jul. 1977-Mar. 78	75	56	49				

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Repeatability of accelerated outdoor exposure tests on alkyd finishes (Phoenix : Emmaqua)

Panel No.	Det	Langleys received*							
	Year and season	80,000 lys.	160,000 lys.	240,000 lys.					
47	1971-72 Winter	86	79	60					
51	1975 Spring	95	87	41					
6	1978 Autumn	95	87	64					

*The irradiation of 240,000 Langleys (1 ly = 1 g cal/sq cm/min) is achieved within 45-60 days depending on the seasonal weather variations.

Table (6	В
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Repeatability of natural outdoor exposure tests on alkyd finishes (Miami : 5°South)

	Dete	Time: Months						
Panel No.	Year and Season	3 Months	6 Months	9 Months				
47	Dec. 1971-Sept. 72	87	72	47				
51	Dec. 1974-Sept. 75	78	64	42				
6	Jul. 1977-Mar. 78	79	66	61				



Fig. 4. Repeatability of accelerated outdoor exposure tests. Phoenix, 1971 to 1972, 1975, 1978. Emmagua











Fig. 7. Repeatability of accelerated and natural outdoor exposure tests on alkyd finishes. Phoenix, Emmagua and Miami, 5°South

Evaluation of results

As seen from the data and the Figures, all the tests ranked the acrylic type No. 5 as slightly superior to the alkyd type No. 6. This agrees well with long practical experience and also with earlier comparative results of Florida and *Emmaqua* tests.

Gloss retention of the two types did not differ substantially, except in case of the QUV exposure.

The same applies to chalking. A slight tendency to chalking of No. 6 was observed both in Miami and on *Emmaqua*, but none in the weatherometer test. However, very definite chalking appeared at an early stage in the QUV tester (after about 72 hours). Practical experience during the past 8 years had never indicated any serious chalking problems with the alkyd system.

Colour retention of the acrylic finish is also somewhat superior. Numerical data were available only for the *Emmaqua* exposure. The colour difference measured for the acrylic was $\Delta E = 1.02$ against $\Delta E = 1.38$ for the alkyd. This slight difference confirms the hardly noticeable visual difference found in case of the other exposures.

Scrutiny of the test methods

Ref. 9

Florida Exposure at 5°South in the present context represents the long term standard test. Exposures performed during a number of years usually rank the same series of coatings in the same order, However, presumably because of climatic variations, results obtained in different years may vary by up to 20 per cent in gloss retention.

Repeated *Emmaqua* exposures show a very similar picture. Occasionally, the seasonal and annual variations are smaller. The course of gloss deterioration, however, is very similar in this indirect outdoor exposure to that occurring in direct outdoor exposure in S. Florida. The acceleration of the process is about 5-6 fold.

Weatherometer exposure for 1000 hours does not lead to any conclusive results. The duration of the exposure is insufficient to cause more than a few percent of gloss deterioration in stoving automotive finishes. Similar results were also obtained in earlier tests⁹.

The QUV Tester gives rapid results, but they occasionally seem to be somewhat distorted. Apparently, the cycle used is very fierce with respect to inducing chalking. Here, Florida and *Emmaqua* exposure, as well as actual practice, hardly indicate any chalking tendency; the stoving alkyd finish chalks badly after a quite short exposure in this test.

Conclusions

It is difficult to draw clear-cut conclusions from such a restricted experiment, but the tests raise certain points which may be helpful when selecting an accelerated weathering test for a project.

(1) Samples have to be prepared with the utmost care and in the best possible manner. Where possible, duplicate panels should be used for each test.

(2) Uniform and precise operation and maintenance of artificial weathering devices are essential.

(3) Whenever new products are tested, a standard product based on a similar binder and of known performance must be included as a control. Various accelerated weathering devices produce different balances of the stresses (light, heat and humidity) which cause the finish to deteriorate and may have a stronger effect on one kind of polymer than on another.

(4) If time and circumstances permit it, the samples should be exposed to at least two different methods of accelerated weathering (eg on *Emmaqua* and in the QUV cyclic tester). The first method takes slightly longer, but being an acceleration of natural outdoor conditions, it will tend to give results which correlate better with long term natural exposure and real life performance.

The QUV test gives fast results, but tends to exaggerate some minor weakness of the product disproportionately.

(5) When evaluating results, the relative importance of any particular property with respect to the overall efficiency of the product should be borne in mind, unless the sole objective of testing is to compare one specific component or a characteristic property of a complex system.

Some relevant publications in 1978

Refs. 10-15

Having evaluated the experimental results from the point of view of the paint chemist involved in development work, the author searched for new developments in this controversial topic which may have emerged in the last year.

1979 (4) ACCELERATED WEATHERING TESTS

Recent papers do not hold out any hope of predicting a coating's durability in exact terms of years (as would be desired for guarantee purposes) on the basis of accelerated weathering tests. However, international experts are beginning to appreciate their merits.

A deeper understanding of the complex interaction of stresses caused by natural weathering and the study of wavelength distribution in solar radiation and its effects in combination with varying moisture and temperature conditions has enabled the early information derived from various accelerated weathering tests to be used to greater benefit.

This latest trend of thoughts is well illustrated by quoting a few recent conclusions.

An analysis of natural weathering¹⁰ in the USA has indicated that the reason for the good correlation found between the exposure results obtained in aggressive environments, such as Florida and Arizona, and the more temperate climates, is the fact that maximum UV, water and temperature stresses are similar everywhere. Elimination of annual, seasonal and location rate differences by mathematical treatment of the results (rank correlation procedure) has made it possible to predict consistently the relative merits of materials by natural accelerated weathering. Modern high quality coatings have a high threshold of sensitivity towards UV, water and heat, and, therefore, natural weathering for such products ceased to be a continuous process. It is sporadic and intermittent, occurring only when the stresses reach a certain level. Simulating basic stresses in artificial weathering, results in acceleration by avoiding idle time. Further acceleration is achieved by increasing the combined UV, water and temperature stresses within natural limits. The most important factor in accelerated laboratory testing is the proper balance between the stresses. This is possible, but there exists no single answer.

A systematic study was conducted in W. Germany to reveal the causes for the discrepancies occurring in consecutive or parallel weathering tests¹¹ in respect of gloss retention and chalking, both in natural and laboratory exposures. Errors arising from the lack of uniformity in sample preparation and those caused by variations in radiation intensity in artificial devices, compensate each other to some extent, but the latter is of much greater importance and has to be controlled as far as possible. The adverse effect of this discrepancy can also be reduced by including reference samples of proven performance in the test of experimental products.

Testing gloss retention and chalk resistance¹² of TiO_2 pigmented finishes after exposure is an important feature of the continuous research into the photochemical interaction between this pigment and binders. In a given resin, the ranking of various grades remains consistent, eg the results obtained on one stoving acrylic system will be valid for another acrylic, but will not necessarily apply to an alkyd based system, or vice versa.

Whilst both characteristics are due to the degradation of the resin, no direct relation has yet been established between loss of gloss and the onset of chalking ¹³. Some resins will chalk at an early stage of loss of gloss, others not even when gloss is down to almost nil.

The chalking rate is greatly accelerated in some of the accelerated tests. Paint systems which repeatedly passed up to 5 years of exposure in S. Florida and over 10 years in Switzerland without any chalking, may fail badly after only 100 hours in a dew-cycle weatherometer. If a film passes this

fierce test, it will most likely perform very well in practice, but its failure does not mean that the system is worthless.

Based on current commercial devices, a special accelerated weathering apparatus has been built in Germany for the study in depth of the chalking process¹⁴. It includes features like a selection of spectral range, of experimental atmosphere (air, argon, nitrogen, vacuum), strict control of temperature and a constant radiation yield.

It is claimed that these studies covered such problems as the effect of wavelength and the nature of the chalking cycle, ie the photochemical interactions which take place during the weathering of TiO_2 pigmented coatings. The protective effect of after-treated rutile TiO_2 pigments is strongest when the absorption boundary of the binder is at a shorter wavelength than that of the pigment.

A West German author has suggested very recently that the evaluation of weathering results¹⁵ can be rendered far more meaningful if the gloss retention and chalking rate data are related to the energy of irradiation in the UV-B (280-315nm) range instead of the period of exposure, as was customary among the continental European experts.

Thus, the results obtained for a given material at the same location at different times, at various stations or in artificial accelerated devices at the same time, can be compared in a realistic manner.

The author fully agrees with the above suggestion, but would like to add that, to her knowledge, the idea is not as new as claimed. This concept has been widely accepted and applied for quite some time in the United States (Langleys represent the solar radiation energy received). Obviously, the method is feasible only if the energy values calculated by factors from global radiation are available.

This survey can be concluded with the thought that in choosing the test methods according to the purpose of the weathering test, the operator must be just as flexible as the surface coatings are expected to be. Just as the ideal paint has not yet been developed, so there is no all-purpose, universally applicable weathering test.

Acknowledgment

The author wishes to thank her colleagues at Ault & Wiborg Paints Ltd, Perivale, UK and at DSET Laboratories, Inc. Phoenix, USA for the preparation of samples and performance of the accelerated weathering tests in artificial laboratory devices and by indirect outdoor exposure to solar radiation.

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Preparation and use of antifouling coatings based on tributyltin fluoride

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Summary

In view of the limited period of protection of cuprous oxide based antifouling coatings in regions of high fouling and the danger of copper accumulation in waters and sediments in semi-enclosed areas, a need has arisen for longer protection periods with less polluting effects. In this paper, tributyltin fluoride is used as an

Keywords

Types and classes of coatings and allied products

antifouling coating

Raw materials for coatings

binders (resins, etc.)

polyvinyl resin

biologically active ingredients

tributyltin fluoride micro biological agent alternative to cuprous oxide in the preparation of a variety of paints intended to provide fouling resistance for long periods. The results of testing in a natural environment of high fouling intensity are very promising with respect to animal organisms, but not so much with respect to plant fouling.

Properties, characteristics and conditions primarily associated with dried or cured films

sea water immersion test

La préparation et l'emploi des revêtements "anti fouling" à base du fluorure de stantributyle

Résumé

En raison del la période restreinte de protection assurée par les revêtements "anti fouling" à base de l'oxyde de cuivre aux régions où le risque de salissure est élevé, et également du danger d'une augmentation progressive de la teneur en cuivre dans les eaux et les sédiments en bassins mi-clos, on a besoin des périodes de protection plus longues et des teneurs en agents polluants moins importantes. Dans cet exposé on a utilisé le fluorure de stantributyle

en tant que remplacement pour l'oxyde de cuivre au cours de la préparation d'une gamme de peintures "anti fouling" destinées à assurer une résistance aux salissures pour de longues périodes. Les résultats des essais dans un environnement naturel, où l'intensité de salissures est élevée, donnent beaucoup d'espérances à l'égard des organismes animaux, mais pas autant en ce qui concerne les salissures provoquées par les plantes.

Herstellung und Anwendung von Antifoulings auf Basis von Tributylfluorid

Zusammenfassung

In Anbetracht der zeitlich begrenzten Schutzwirkung von auf Kupferoxydul basierenden Antifoulings in stark foulenden Gewässern, sowie der Gefahr von zu hoher Kupferkonzentration in Gewässern und Sedimentation in halbabgeschlossenen Wasserlaufen wurde es nötig, einelänger schützende Farbe mit geringerer Pollutionswirkung zu entwickeln. In dieser Arbeit wurde Tributylzinn-

Introduction

Refs. 1-7, 18

In a previous publication¹ dealing with antifouling coatings depending on vinyl resins as binders and cuprous oxide as the toxic pigment, it was found that the maximum period of protection in fouling-rich regions was thirteen months. It was suggested that further research should be directed to the use of other binder systems and to higher efficiency toxins which may supplement or replace cuprous oxide: This trend has been prompted by recent investigations² in which the copper concentration was found to be two orders of magnitude higher than the natural limit in the waters and sediments of the Suez Canal. This threatening level was solely attributed to copper leached from ships traversing the international pathway at a rate estimated at 3000 vessels per fluorid als ein Alternativum für Kupferoxydul zur Herstellung einer Anzahl von Antifoulings mit lauganhaltender Schutzwirkung angewandt. Die Ergebnisse von Versuchen in natürlichen, stark foulenden Gewässern sind vielversprechend bei tierischen Organismen, nicht aber bei Pflanzenanwuchs.

month. The phenomenon of increased copper levels was also observed in other places, such as the harbours of Antibes, La Pallice and La Rochelle in South France³ which was attributed to the great number of pleasure boat using copper and cuprous oxide antifouling coatings. High copper concentrations were also found in the waters of the docking areas of San Francisco Bay⁴. The same author found copper contents in abundant marine algae, Ulva sp. ranging from 10.6 to 43.4 $\mu g/g$ tissue (dry weight). Further alarm was caused by a paper by Disalvo⁵, in which the effect of copper on the survival and functioning of the lower, important organisms, the bacteria, was examined. The results indicated the variable susceptibility of bacteria to the presence of copper and suggested the possibility of cumulative synergistic effects of heavy metals on bacterial motility. It was estimated that 5000 tons of copper are released annually from copper based antifouling coatings in the oceans and seas of the world⁶.

In the present investigation the binder mixture, based essentially on a vinyl copolymer, was kept constant, whilst cuprous oxide was replaced entirely by one of the recently developed organotin compounds. Trialkyl- and triaryltin compounds are gaining ground since their fungicidal effects were discovered in 1954. They were recommended for antifouling applications because of their slow, but effective release of tin and for their long periods of protection (reaching two years) and because they do not accelerate corrosion. A case of a protection period of 92 months, where the tributyltin compounds were included in a thick rubber sheet has been documented⁷.

The type of plasticiser used with the vinyl binders was shown to play an important role in antifouling coatings in which cuprous oxide was the toxic ingredient¹; the chemical composition of the plasticiser controls the leaching rate of copper and hence the prevention of fouling in long term environmental immersion. The present investigation includes the use of three different types of commercial plasticiser: (1) hydrolysable, (2) non-hydrolysable and (3) non-hydrolysable but swellable plasticiser, in order to examine their role in conjunction with tributyltin fluoride as the toxic ingredient.

Whilst it was hoped to conduct the environmental testing for a much longer period, the test was terminated after 211 days due to a sudden storm which sank the raft. However, the photographic recording of the last inspection provides evidence of further protection periods. The test period, however, exceeded a period of 6 months suggested for a successful antifouling coating in the Egyptian Standard Specifications¹⁸.

Materials

The vinyl copolymer was Laroflex MP 35 (BASF AG, Ludwigshafen, Germany). The plasticisers were: chlorinated paraffin (non-hydrolysable) N 50 (Farbwerke Hoechst AG, Germany), tritolyl phosphate (hydrolysable) and polyvinyl methyl ether (non-hydrolysable but swellable) (Lutonal M 50 of BASF AG). The modifying resins were ester gum (Carless Capal, England) and a phenolic resin, Wresnyl 265 (Resinous Chemicals, England). Thixtrol ST, a hydrogenated castor oil was used as anti-settling agent (BASF, AG).

Tributyltin fluoride was supplied by Berk, Co. Ltd, England.

Titanium dioxide was of the rutile type (Titangesellschaft, AG, West Germany). Iron oxide was of the type 130 F

(Farbwerke Bayer, AG, Germany). China clay was obtained from English China Clays, England.

Suitable mixtures of xylene, white spirit (145-185°C), butyl acetate and butanol were used as solvents.

Methods

Paint preparation and composition

Refs. 8-11

Batches of 300 g each were prepared by mixing the correct amounts of the ingredients. The mass was matured and then dispersed in a centrifugal ball mill. The paints were diluted to the application viscosity using a suitable blend of solvents, filtered twice and stored in tins with air-tight lids in a cool place. The storage time before application ranged between two and four weeks; the paints were, however, free from settlement or any other defects after several months of storage.

Ten paint compositions were prepared with a common binder mixture containing mainly a neutral vinyl copolymer. A slight acidity is provided by a small amount of ester gum resin (acid number 3-5 mg KOH/g) and some improvement of hardness is given by a small content of a phenolic resin. A traditional constituent in antifouling coatings, rosin, is absent from all formulations. It was established long ago that rosin plays an important role in the performance of both soluble-matrix and contact-leaching copper antifouling coatings. In trialkyl- or triaryltin compounds, the mechanism is believed to be one of slow-release which does not depend on the dissolution of rosin, but rather on migration of particles of the compound from the interior of the coating to its surface and then to the water⁸.

Tributyltin fluoride was introduced in the formulations in four different ratios, namely, 15, 20, 25 and 30 per cent by weight of the total dry film. Values suggested in some of the small amounts of literature available^{9,10} on tributyltin fluoride antifouling coatings range between 16-20 per cent; values in the range 30-40 per cent are given in other literature¹¹, but this is thought to be impracticable. The wide range used in the present work is intended to meet the severe fouling conditions at the testing site. Talc and china clay were included in substantial amounts, not only to improve paint properties, but also for their favourable surface characteristics on the rate of release of the toxic ingredient. The coating compositions are given in Table 1 which also includes a

Dry film composition of antifouling coatings										
AF. No.	1	2	3	4	5	6	7	8	9	10
Vinyl copolymer Polyvinyl methyl ether Chlorinated paraffin	15 4.5	15 4.5	15 4.5	15 4.5	$\frac{17}{1.7}$	$\frac{17}{1.7}$	17 	16 	16	16
Tritolyl phosphate Phenolic resin Ester gum	3 2.5	3 2.5	3 2.5	3 2.5	3.3 3	3.3 3	3.3 3	2.5 3.2 3.4	2.5 3.2 3.4	2.5 3.2 3.3
TBTF Iron oxide red Titanium dioxide	15 14 20	20 14 20	25 14 20	30 14 20	20 14 20	25 14 20	30 14 20	20 14 20	25 14 20	30 14 20
Talc China clay PVC	15 11 58	10 11 60	5 11 61.6	11 63.0	10 11 60.5	5 11 61.9	11 63.4	10 11 60.2	5 11 61.9	11 63.3
I oxin volume concentration	24	51	37.3	43	51.5	57.4	43.2	51.5	57.4	43.1

Table 1 Dry film composition of antifouling co

calculation of the total pigment volume concentration and the toxic (pigment) volume concentration.

Test panels

Sheets 3 mm thick of pigmented impact-resistant polystyrene were cut to panel dimensions of 20×15 cm. The edges were tapered and the surfaces were coated with a thin layer of an epoxy paint, left to dry and then roughened with sandpaper. The use of plastic panels was intended to avoid interference by corrosion and probable complications of incomplete compatibility with the anticorrosive layer.

The panels were coated (in duplicate) front and back with two successive coats at an interval of 6 hours drying between the two coats. The average film thickness was 90 $\mu m \pm 10 \,\mu m$. Particular care was taken with the edges to eliminate pores and weak points.

The coated panels were connected to boat-like cages with nylon threads through holes bored in the panels. Each composition was represented by two panels; one placed in a vertical position and the other at 60° to the horizontal.

Environmental exposure

Refs. 12, 13

The cages were submerged in the testing area of the raft¹² in Alexandria Eastern harbour on 24 May at a depth of about 150 cm from the surface. Periodic visual and biological examination and photographic recording of the condition of the panels were performed. The region is known for abundant fouling organisms almost throughout the year; there are reasons to believe that the rate of growth of most fouling organisms has doubled since an extensive survey was concluded by Ghobashy¹³ in 1975. Periodic testing of water salinity, temperature, and pH was performed.

Results

Refs. 1, 14-17

All coatings were completely intact and free from fouling at the end of the first two months of immersion. The general feature was the formation of slime and attachment of slight algal growth. Only a few individual barnacles were observed at the edges and around the holes of the panels due to bare points and some detachment of the coating during manipulation.

From the beginning of the third month until the test was terminated, the intensity of the slime film on all plates was moderate, but the films tended to be thicker on coatings with lower contents of the tin compound. No serious attack on the test panels by barnacles, tube worms or other foulers was observed throughout the whole period of immersion of 211 days. Small scattered settlements took place at the edges only.

A photographic record of the test is shown in Figure 1. The great contrast between the cleanliness of the coated panels and heavy fouling on the supporting cage is clearly seen. The latter carried such heavy loads of barnacles and tube worms, reaching 12 to 15 cm in thickness at the last inspection, that parts of the test panels area were hidden behind the intensive growth. Continuation of the test would have left very little room for comparison of the individual formulations for their relative long-term efficiency, because of encroachment of fouling. A new design of supporting frames providing larger space between the test panels and other objects was developed and used¹.

The test period (211 days) was either too short to provide differentiation between the plasticiser types or to show that the protective function, in the case of organotin compounds, is independent of the chemical nature of the plasticiser in contrast to cuprous oxide formulations whose antifouling function was lost much earlier than the aforementioned period when a non-hydrolysable plasticiser was used14. The second postulation is more plausible and supports the view that the mechanism of protection by organotin formulations depends on the ability of the toxic particles to diffuse from the interior of the film to its surface. This diffusion is controlled by the texture and configuration of other components of the coating15, rather than on the swellability of the plasticiser¹, or the solubility of other components such as rosin. The postulation of slow release is supported by the test results which are independent of the type of plasticiser and by the fact that the compositions are effective without rosin as a seawater-soluble component.

One of the disadvantages of slow-release organotin formulations is their very short range of protection; the repellancy to fouling larvae takes place in the immediate vicinity of the surface, in contrast to copper formulations which leach out a soluble toxic layer over a much wider range. Full protection of the edges and corners was, therefore, much more difficult with organotin formulations than with their copper counterparts.

Another drawback is the ineffectiveness of organotin formulations on plant fouling organisms relative to the copper formulations. Although brown algae were detected in the present series, serious plant fouling did not occur because the experiment was terminated before the season of plant growth which begins early in the spring; plant fouling was detected and characterised in a later series¹⁶. One of the solutions to this drawback is to use combined cuprous oxide-organotin formulations¹⁷.

Conclusions

Ref. 18

Coatings based on vinyl binders containing 15-30 per cent by weight tributyltin fluoride are effective antifoulants and satisfy the standard specifications¹⁸ of six months protection in natural environment. They function by a slow-release mechanism which is independent of the presence of a soluble ingredient, and thus their effective life-time is prolonged in comparison with compositions based on cuprous oxide as the toxin and rosin as the soluble ingredient. A further advantage of the former lies, presumably, in their less hazardous effects on marine ecology, particularly in harbours and narrow waterways. The economies seem favourable because of the increasing production of organotin compounds.

Acknowledgment

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The authors are also indebted to BASF AG, Ludwigshafen for provision of starting materials of their own and other



Fig. 1. Environmental testing of TBTF antifouling coatings in Eastern Harbour of Alexandria

companies' products, and for useful discussions with Drs Neubert, Brussmann and Morcos of AWETA (Applied Research Department) of BASF AG.

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Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the May issue of the *Journal*:

The reaction of epoxy side groups in polymers and amines-Influence of solvent and additives by S. Paul and B. Rånby

Lung cancer mortality of workers in chromate pigment manufacture: An epidemiological survey by J. M. Davies

The automatic cleaning of tanks, tankers and plant by high pressure spray by W. Hirzel

Film characteristics of polyepoxide resins based on novolac resins by A. K. Vasishtha and V. K. Kaushal

The efflorescence resistance of certain emulsion coatings by J. Boxall and W. Worley

Section Proceedings

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Solvent recovery

On 16 February, Mr I. Smallwood of Fraser McNaughton Ltd presented a very topical lecture entitled "Solvent recovery in the paint industry".

Mr Smallwood outlined the various options open to the paint and ink maker for disposing of used solvents, beginning with the non-recovery techniques such as:

Dumping: this is becoming increasingly difficult as the solvent must be emptied out of the barrels and the saturated soils then buried.

Incineration: some solvents can be used to produce high temperatures from commercial incinerators.

As a useful boiler fuel: here pigment must be removed and the boiler converted. Mr Smallwood outlined the tests done and the specifications for such fuels, with particular regard to chlorinated solvents. The legislation concerning excise duty was also discussed.

As a motor fuel blending stock: this has become economically attractive in the last year or so. It is necessary to remove both pigment and resin and the yield is, therefore, lower but the price correspondingly higher.

Mr Smallwood then went on to discuss the solvent recovery operations, resulting in a product which can be used again either as a prime solvent or as a cleaning solvent. He explained in some detail the type of equipment required for steam distillation and hot oil distillation, giving examples of throughput yields and costs, both as small "do it yourself" installations and the large solvent recovery contractors' plant.

Everyone present found it to be a very well presented and stimulating lecture, the lively discussion which followed being indicative of the interest in this subject.

D.P.

Manchester

Inks for packaging

A near record total of 150 members and visitors attended a joint lecture with the Institute of Printing, North Western Branch at the Woodcourt Hotel, Sale on Monday 5 February 1979. Mr H. J. Duffin, Sales Director of Irlam Inks Ltd, revealed that his 27 years experience in printing inks were initially as a chemist before becoming a salesman. Health and safety was the first subject covered, pointing out that printing inks were not guaranteed as suitable for direct contact between ink and foodstuff. The second subject discussed in detail was the four methods of application, namely, letterpress, offset lithography, gravure process and flexography, combined with reference to plate/roller choice and the four basic colours encountered, yellow, magenta, sian and black.

Mr Duffin then discussed printing on films in flexible packaging such as cellulosic, polyvinyl chloride, polyolefins, aluminium, polyester etc. Pigments/dyestuffs selection was noted, the choice dictated by lowest cost in relation to resistance requirements.

Logical progression continued with the discussion of binder choice which included such diverse types as oxidising, UV cured acrylics, nitrocellulose, polyamide, shellac, rosin/ maleic, cellulose acetate propionate and ethyl-cellulose.

The choice of solvents is influenced by many factors which include cost, evaporation rate, solvation characteristics, effect on roller/plate etc.

Mr Duffin concluded his lecture by the use of colour slides illustrating Production and Development/Quality Control facilities at his factory.

A vote of thanks was proposed by Mr John George, Chairman of the N.E. Branch I.O.P., which was unanimously acknowledged.

F.B.W.

Newcastle

All our yesterdays

The fifth meeting of the 1978/79 session was held in St Marys College, Durham, on 1 February when, at short notice, Mr F. Hellens, Chairman of the Section, presented a paper entitled "30 years in the paint industry". Some 30 members and guests assembled for the presentation and the Chairman especially welcomed Mr F. B. Windsor, Publications Officer of the Manchester Section.

The Chairman's period in the paint industry covered the years 1947–1979, although he was quick to point out that having spent two years in "beds" the title of his talk was mathematically correct. With reference to computers, stock control, comics and even striking bus drivers, the Chairman amused and amazed his audience in recalling his exploits. On a more serious note it was worth noting the number of company names which had disappeared during the 30 year period with a consequent loss in jobs and hence a decline in Section membership. Mr Hellens then gave a brief resumé of the OCCA Exhibition and its value to the individual member.

Turning to the future, the Chairman forsaw success for a number of small firms now located within the area, but the fate of some of the larger companies was not so certain. Mr Hellens thought that the paint industry moved in 30 year cycles and reminded us of the large number of small companies in existence 30 years ago who had merged or been taken over to form the larger companies of today. Bearing this 30 year cycle in mind is it possible that a second Frank Hellens is lurking, unsuspected in someone's laboratory?

Following a lively discussion period, members and guests partook of the buffet and bar facilities.

T.H.

Information Received

UK agency

Bowerhill Engineering Ltd, a member of the Tower Silos Group of Companies, has announced an agreement with Silos Parcey of France for the sole UK and Eire manufacturing rights to their range of silo discharge equipment.

The equipment works in conjunction with flat bottomed silos and storage vessels of up to 20 metres diameter and is claimed to be unique in the industry in that it incorporates features which provide uniform extraction from the total base area of the storage unit, thus ensuring stock rotation.

New products

New purging material

Industrial Science Ltd has announced the introduction of a new purging material called Dalpurge, a non-toxic powder which is mixed with the incoming raw material and processed through either an injection moulding, extrusion or blow moulding machine. Dalpurge is claimed to be effective in removing all thermo plastics or rubber from screws, barrels, etc. and has the advantage that only a small quantity is required to effect a successful purge.

New diverter valve

A new range of diverter valves for use in systems handling powders and granules, said to be a compact construction, has been introduced by Bush & Wilton Valves Ltd. Known as the Flocontrol Series 80, the range comprises four inlet sizes of 150, 200, 250 and 300 mm square. The design allows material to flow from the inlet branch and independently down either outlet duct, giving complete dust-tight shut-off to either or both.



The new diverter valve from Bush & Wilton

Microprocessor-based titration system

Metrohm of Switzerland has developed an automatic microprocessor-based titration system named the E636 titroprocessor which offers fully automatic operation in chemical titrations with full calculator facilities.

New weighing system

Promtek Ltd has recently introduced an add-on Weighing Control for their micro processor based PAC 85 Process Controller. The new attachment is described as a sophisticated weigher control, the extra

The new weigher control system is claimed to be very flexible, covering cumulative and non-cumulative weighing of multiple ingredients.

Corrosion test cabinet

Westlairds Ltd, the UK representatives of H. G. Koehler of Germany, have announced that the well-known Kesternich SO_2 corrosion Test Cabinet has been re-designed to include facilities for salt spray testing.



The re-designed test cabinet from Koehler

Basantin colours

BASF has introduced a new range of pigment dispersions in a solvent-free hydrocarbon resin which is soluble in white spirit. Basantin colours can be easily dispersed in aliphatic and in aromatic hydrocarbons, alkyd resin solutions, etc. and can be used for pigmenting transparent wood preservatives and protective varnishes.

Also recently introduced from BASF is Acronal 18D, a finely dispersed aqueous acrylic homopolymer dispersion for the production of paints and textured finishes. It has a good pigment binding capacity and produces coatings with high resistance to water and alkali with good exterior exposure performance.

New prepolymers

The Chemical Division of Degussa has developed a number of prepolymers and reactive thinning agents for use in irradiation-curable systems. At present, the Degussa range consists of the prepolymers VP S 1928, VP S 1748 and VP S 2700, and the reactive thinning agents ethyl diglycol acrylate, tripropylene glycol diacrylate, tripropylene glycol diacrylate, tripropylene glycol diacrylate, triacrylate and pentaerythritol triacrylate. Other multi-functional acrylates are in the laboratory development stage and can be supplied on request.

New Permuthane coatings

A new range of Permuthane aqueous polyurethane dispersions has been introduced by Stahl Chemical (GB) Ltd. The nonflammable dispersions result in low-pollution levels and produce coatings which have the toughness and abrasion-resistance of polyurethanes.

Versatile filling machine

Neumo Ltd has available its latest modular constructed, mobile, semi-automatic filling machine for handling foaming and nonfoaming liquids of various viscosities. The air-operated machine is capable of top and bottom filling containers from 250 mm to 5 litres and above with instant change of volume of product dispensed.

New digital thermometer

Channel Electronics (Sussex) Ltd has introduced the L520 series pocket size digital thermometer designed for fast and reliable measurement of temperature in the range -150°C to 1150°C.

Proportion mixer

M. G. Electric (Colchester) Ltd has announced the introduction of the Models 2080 (6 per cent) and H6V12P (10 per cent) Proportion Mixers and Systems, which are water-driven chemical piston proportioners which automatically dispense solutions at selected concentrations. Water passing through the cylinder operates the injector unit and as the piston is operated concentrate is drawn and injected at a predetermined rate back into the water flow on the outlet section of the unit.

Conferences, courses, etc.

British Standards

The British Standards Institution have recently published the following:

BS 3900. Methods of test for paints. Part E10. Pull-off test for adhesion, which specifies a method for assessing the adhesion of paint by measuring the minimum tensile stress necessary to detach or rupture the coating in a direction perpendicular to the substrate.

BS 5497. Precision of test methods is a basic reference standard to be used as an aid to the quality control of bulk commodities and is issued complete with a computer programme for ease of application.

XVth FATIPEC Congress

The XVth FATIPEC Congress will be held from 8–13 June 1980 at the International Congrescentrum RAI in Amsterdam with the theme "Activities of the coatings industry in the framework of ecology, energy and economy problems".

Patent information

The Paint Research Association has available an article entitled "Patents, patent information and the paint industry" by Dr L. A. O'Neill, which is a survey covering the new legislation, information retrieval and economic trends within the industry.

Corrosion control

The National Association of Corrosion Engineers, USA, is organising a Symposium on "Corrosion control by organic coatings" to be held at Lehigh University, Pennsylvania, from 11–15 August 1980.

Notes and News



The next OCCA biennial Conference will be held at the Stratford Hilton Hotel, Stratford-upon-Avon, Warwickshire from 20-23 June 1979. The theme for the Conference will be all aspects of the challenge of new materials and the substitution of traditional ones, new methods of construction and the problems of application and the effects of new legislation on coatings during the last quarter of the twentieth century.

A list of the papers to be presented together with their summaries and biographies of the lecturers was published in the December 1978 issue of the *Journal* and copies of the Conference brochure and registration form were enclosed in all copies of the *Journal* sent to Members attached to the General Overseas Section and nonmember subscribers to the *Journal*.

The brochures are being sent to all Members attached to the UK and Irish Sections with Section circulars. Any nonmember who has not yet received a copy of the brochure and wishes to register for this important Conference should apply for the necessary form to the Association's offices. Non-members wishing to avail themselves of the preferential Conference fee for Members may do so by sending in a membership application form at the same time

A view of Anne Hathaway's Cottage, situated close to Stratford-upon-Avon, which contains a museum of Shakespearian articles

as they submit their Conference registration form and the fee enclosed should cover both the membership entrance fee, 1979 subscription and the Conference registration fee. Membership application forms can be obtained from the Association's offices. The registration fees for the Stratford Conference will be £60 (plus value added tax at the standard rate) for Members, £80 (plus VAT) for non-members and £20 (plus VAT) for wives. A daily registration fee for Members of the Association of £35 (plus VAT) and of £20 (plus VAT) for Registered Students of the Association has been set.

Preprints of the papers are now being prepared and it is expected that these, together with details of accommodation, badges, programmes etc. will be sent to those who have registered in May 1979. It is a feature of the Association's Conferences that preprints are sent well in advance of the function in order to enable delegates to read them before the Conference, at which the lecturers illustrate their topics but do not read their papers in their entirety. This allows for a much longer discussion period than at many other conferences and has proved of immense value to those attending previous Association Conferences.

Stratford-upon-Avon new is a venue for the OCCA Conference and it is expected that it will prove popular and interesting to delegates. A full social programme has been arranged for the benefit of those attending the Conference including delegates' wives and this includes coach parties to local places of interest including Makespeare's birthplace, Warwick Castle and Oxford, and also a golf tournament and theatre party to the Royal Shakespeare theatre.

Further information may be obtained from the Director & Secretary at the address on the Contents page of this issue (Tel: 01-908 1086; Telex 922670).

Report of Council Meeting

A meeting of Council took place at the Great Northern Hotel, London N1 on 14 February 1979 with the President, Mr A. McLean, in the chair. There were 25 members of Council present.

Before commencing the meeting the President asked the Council to stand in silent tribute to the memory of two distinguished members of the Association whose deaths had been reported since the last Council meeting-Dr H. A. Hampton (President 1961-1963) and Mr A. McWilliam, who at the time of his death had been Chairman of the Manchester Section.

The Annual Report of the Council for 1978 was approved, together with the Agenda for the Annual General Meeting which will take place on 22 June 1979.

Reports were received on the arrangements for the Stratford-upon-Avon Conference (20-23 June 1979) and Council was saddened to learn of the death of Dr H. Gerhart, who had been nominated by the Federation of Societies for Coatings Technology to present a paper on its behalf.

It was unanimously agreed that any member whose subscription was three months in arrears would not receive the April issue of the *Journal* and would not be entitled to copies of the *Journal* published during the period of arrears.

It was reported that there were well over 100 organisations from 15 countries participating at the forthcoming OCCA-31 Exhibition and that copies of the "Official Guide" would be despatched to members early in March. Arrangements had been made to hold an informal luncheon on the opening day to which the principal officers of other societies and government departments had been invited.

It was reported that a meeting of the Exhibitors' Liaison Group with members

of the Exhibition committee had taken place on 9 February.

Details of proposed Section Symposia were recorded and further details will appear in the *Journal* from time to time.

It was reported that at a meeting of the Professional Grade Committee held earlier in the day, one Fellow had been admitted, one Associate had been transferred to Fellowship, four Associates admitted and one Licentiate transferred to Associateship. In addition, it was reported that two Licentiates had been admitted as a result of successfully completing their viva voce examinations.

Council noted with pleasure that a letter had been received from the Secretary of the Society of British Printing Ink Manufacturers stating that the Technical Training Board of the Printing Ink and Roller Making Industry had passed a resolution recommending to their Members that encouragement be given to their staff wherever possible to apply for admission to the Association's Professional Grade.

The Sections reported on other activities and it was noted that considerable progress had been made with the outstanding item on the proposed New Zealand Division constitution.

The Newcastle Section Committee re-corded its thanks to the Council for the Commendation Award made to Mr H. Fuller.

A full report was given of the recent visit to the UK of the South African Vice-President, Mr P. A. J. Gate, who had dis-cussed items of interest to the Division with the Director & Secretary

As a result of the successful Student Symposium, organised by the Eastern Branch of the Scottish Section, 43 registered students of the Association had been enrolled.

Reports were received on overseas liaison, it being noted that the next FATIPEC Congress would take place in Amsterdam, 8-13 June, 1980 and that the next Conven-tion of the Federation of Societies for Coatings Technology would take place 3-5 October, 1979, at St. Louis.

Professional grade

At a Meeting of the Professional Grade Committee held on 14 February 1979, the following Ordinary Members of the Association were admitted to the categories shown. The Section to which each Member is attached is shown in brackets.

Fellow

Bosman, Herman Izak (Transvaal)

Transferred from Associate to Fellow

Morris, David (London)

Associate

Craske, Anthony John (General Overseas-Indonesia)

Register of Members

The following elections to membership have been approved by Council. The Section to which each new Member is attached is given in italics.

Ordinary Members

- ADSHEAD, FREDERICK MICHAEL, Ciba-Geigy Pigments Division, Roundthorn Industrial Estate, Wythenshawe, Manchester M23 9ND. (Manchester)
- ARMSTRONG, ROBERT ELLIOTT, Bayer SA (Pty) Ltd, Wrench Road, Isando, Johannesburg 2000, South Africa. (Transvaal)
- BLECH, STEPHEN HARVEY, BSc, 6 Francklyn Gardens, Edgware, Middlesex HA8 8RY. (London)
- CHAN, LAP SHUN, BTech, GRIC, 163 King's Road, 10th Fl. Flat D, North Point, Hong Kong. (General Overseas)
- CHRISTIE, ROBERT MATTHEWS, PhD, BSc, Ciba-Geigy Pigments Division, Hawkhead Road, Paisley, Renfrewshire. (Scottish) COBB.
- B, DAVID MALCOLM, 30 Cross Field Drive, Radcliffe, Manchester M26 0RX. (Manchester)
- DARKE, ANTHONY HAGEN, BSc, 37 Jubilee Road, Middleton, Manchester M24 2LT. (Manchester) DAVIDSON, PETER JOHN, BSc, DPhil, Protim Ltd, Fieldhouse Lane,
- Marlow, Bucks SL7 1LS. (Thames Valley)
- DIVER, GUY ROPER, A R Gibbon Ltd, 3, Highview Road, South Normanton Industrial Estate, Derbyshire. (Midlands—Trent Valley Branch)

There being no other business, the Presi-dent thanked Members for their attendance and declared the Meeting closed at 3.55 p.m.

Obituaries

Desmond Metcalf

An associate member of the Irish Section, Des Metcalf, died suddenly on Saturday 31 January 1979 at the age of 52.

This unexpected and tragic occurrence happened only a short while after the announcement in the Journal of his joining the Board of ICI Ireland Ltd.

Des joined ICI in Dublin in 1945, and following his appointment as a Repre-sentative in 1949, was seconded in 1965 to Associated Irish Gases (an ICI Ireland Associate Company) as Marketing Manager and subsequently General Manager.

He returned to ICI Ireland in November 1969 as Assistant Manager, Chemicals Department, and became Manager of the Department in 1973. In 1978 he joined the Board of ICI Ireland Limited, and at the same time became Chairman of Hilton Products (an ICI Ireland subsidiary), as well as a Director of Associated Irish Gases Limited

A keen sportsman, he played hockey for Ireland, and was an excellent cricketer, and more recently a very proficient golfer and a prominent member of the Castle Golf Club in Dublin.

John Hanrahan, Chairman of ICI Ireland Limited, speaking of the tragic loss said, "apart from his undoubted skills as a businessman, Des Metcalf was a true and well loved friend of many people in ICI Ireland and in several UK Divisions. His gentle humour and considerate style are two of the key qualities for which we shall miss him most".

He leaves a wife and three children to whom we extend our sympathy.

RCS

J. E. Judah

J. E. Judah, an Ordinary Member of the Association, died on 1 February 1979, after a period of illness.

He joined the London Section in 1963, transferring to Hull in 1972. He had served on the Hull Section Committee and was a regular attender of all the Technical and Social functions of the Section until his transfer back to London in February, 1978.

All his friends in the Hull Section extend their deepest sympathy to his wife Nita.

Gilliam, Brian Frederick (London) Hardie, Ian William (London) Toovey, John (Scottish)

Transferred from Licentiate to Associate

Downham, Stephen Airey (Manchester)

Licentiate

Asiedu-Dompreh, Jonathan (London) Leonard, Michael William (London)

LATEANO, JOHN, BSc, Flat 2, 28 Margery Park Road, Forest Gate, London E7 9JY. (London)

- MCCALLUM, SANDRA JENNIFER, YWCA, Alexandra Residential Club, St. Johns Road, Altrincham, Cheshire. (Manchester)
- MOUNTAIN, CHARLES MAURICE, BSC, Mobil Oil SA (Pty) Ltd, PO Box 1043, Johannesburg 2000, South Africa. (Transvaal)
- SCHNELL, ALLEN DOUGLAS, BSc, Snell Chemicals, PO Box 494. Johannesburg, South Africa. (Transvaal)
- WILLIAMS, DAVID, MA, DPhil, BTP Tioxide Ltd, 10 Stratton Street, London W1A 4XP. (London)
- WILLIAMS, JOHN DAVID, 58 Glenavon Road, Prenton, Birkenhead L43 ORF. (Manchester)

Associate Members

ADEGBILE, NOAH ADEREMI, 11 Walmer Crescent, Glasgow G51 1AT. (Scottish)

- ADEOSHUN, CLETUS FRANCIS, 45 West End Park Street, Glasgow G3 6LJ. (Scottish)
- ADINDU, NWACHUKWU HARRY, 1192 Argyle Street, G3 8TE. Glasgow (Scottish)

AKANJI, SHAKIRU-OLALEKAN, 74 Chancellor Street, Glasgow G11 5PN. (Scottish)

ARGENT, VINCENT, The Cottage, Cornsay Colliery, Co. Durham. (Newcastle)

- BUCHLING, FRANS JOHANNES DANIEL, Liba Paint Manufacturers (Pty) Ltd, PO Box 564, Krugersdorp 1740, South Africa. (Transval)
- FABUYI, JOSEPH ABIMBOLA, 45 West End Park Street, Glasgow G3 6LJ. (Scottish)

HARRISON, LESLIE, 6 Rimmington Road, Liverpool L17 0BD. (Manchester)

IKHARO, ABDUL HENRY, 138 Fergus Drive, North Kelvin G20. (Scottish)

KANU, FRED DIXON, 1192 Argyle Street, Glasgcw G3. (Scottish) MACFARLANE, IAN MALCOLM, PO Box 14079, Verwoerdburg 0140, South Africa. (Transvaal)

Registered Students

ANDERSON, NEIL IAIN, 3 Kinneil Place, Hamilton. (Scottish) BAGEN, KENNETH, 54 Mossgiel Avenue, Rutherglen, Glasgow. (Scottish)

- BARCLAY, ANDREW WILLIAM, Ault & Wiborg Ltd, 412 Hillington Road, Glasgow. (Scottish)
- BATES, COLIN, 14 Melbourne Avenue, Stretfield, Manchester M32 0DE. (Manchester)
- CAMERON, GRAHAM HUGH, 12 Garngaber Avenue, Lenzie, Kirkintilloch, Glasgow G66 4LJ. (Scottish)

CASSIDY, BRIAN, 101 Neilsland Oval, Pollok G53 5EN. (Scottish)

- CONDON, DEREK ANTHONY, 15 Merlin Avenue, Bellshill, Lanarkshire ML4 1JY. (Scottish)
- DEMARCO, GEOFFREY, 79 Whittinghame Drive, Jordanhill, Glasgow. (Scottish)
- DONALDSON, WILLIAM, 188 Landemer Drive, Rutherglen, Glasgow G73 2TD. (Scottish)
- DOUGLAS, ALEXANDER, 65 Whitelaw Road, Dunfermline, Fife. (Scottish—Eastern Branch)
- EJEKWU, BONIFACE CHUKS, 83 West Graham Street, Glasgow G4 9LL. (Scottish)
- FINGLAND, DAVID RONALD IAN, 149 Broomhill Drive, Glasgow. (Scottish)
- HEARD, COLIN MCKENZIE, 3 Spynie Place, Lossiemouth, Morayshire. (Scottish)
- HENDERSON, MAIRI CHRISTINE, 44 Canniesburn Road, Bearsden, Glasgow. (Scottish)

HUME, DAVID, 37 Morrison Avenue, Stevenston, Ayrshire.

- IGUNNU, LAWRENCE KAYODE, 70 Ashley Street, Glasgow G3 6HW. (Scottish)
- JOHNSTON, STEVEN JAMES, 21 Stonelan Towers, Burnside, Rutherglen. (Scottish)
- JOHNSTONE, DAVID IAN, 1 Whiteholme, Parkway, Bramhall, Cheshire SK7 3DH. (Manchester)
- JOHNSON, SIMON OSBORNE, 37 Grosvenor Road, Altrincham, Cheshire. (Manchester)
- LAFFERTY, PAUL JAMES, 82 Wellshot Road, Shettleston, Glasgow. (Scottish)
- MACFADYEN, COLIN IAIN BUCHANAN, 41 Muirton Drive, Bishopbriggs, Glasgow. (Scottish)
- MCCOLE, MICHAEL GERALD, 106 Albert Road, Glasgow G42 8DR. (Scottish)
- McCluskey, John, 2 Stonehall Avenue, Hamilton. (Scottish) McCreADIE, EDWARD HATCH, 19 Ledmore Drive, Glasgow G15 7DR
- 7DR.
 (Scottish)

 McGHIE, ROBERT, 21 Broom Terrace, Johnstone.
 (Scottish)
- MACKIE, STEPHEN JAMES, 16a Craigpark, Dennistoun, Glasgow. (Scottish)
- MITCHELL, STEPHEN, 5 Craigmarloch Avenue, Balmore Park, Torrance, Nr. Glasgow. (Scottish)
- Morrison, Alexander John, Ault & Wiborg Ltd, 412 Hillington Road, Glasgow. (Scottish)
- MURRAY, IAN HAMILTON, Usher-Walker Ltd, Canal Street, Kirkintilloch. (Scottish)
- NICHOL, CAMPBELL WILLIAM, 24 Tanzieknowe Drive, West Greenlees, Kirkhill, Cambuslang, Glasgow. (Scottish)
- OHENE, THEODORE SHEALTIAL, 106 West Princes Street, Glasgow G4. (Scottish)
- OLAKUNBI, JANET OLUFUNKE, 231 Kingsacre Road, Rutherglen, Glasgow G73 2EN. (Scottish)
- RAE, DAVID, 61 Keystone Quadrant, Milngavie, Glasgow G62 6LP. (Scottish)
- RICHARDS, KENNETH REA, 95 Townhill Road, Dunfermline KY12 0BS. (Scottish)
- ROOK, LAWRENCE, 37 Dunure Road, Alloway, Ayr. (Scottish) THOMSON, MATTHEW, 24 Craignethan Road, Whitecraigs, Glasgow. (Scottish)
- WATT, GRAEME MACLEAN, 19 Smith Quadrant, Coatbridge. (Scottish)
- WILSON, GERARD, Ault & Wiborg Ltd, 412 Hillington Road, Glasgow. (Scottish)

Forthcoming Events

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the month following publication and in other parts of the world up to the end of the second following publication.

April

Monday 2 April

Hull Section: Annual General Meeting at the George Hotel, Land of Green Ginger, Hull, commencing at 6.30 p.m.

Tuesday 3 April

West Riding Section: Annual General Meeting at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

Thursday 5 April

Newcastle Section: Annual General Meeting at St. Mary's College, Elvet Hill Road, Durham, commencing at 6.30 p.m.

Friday 6 April

Midlands Section-Trent Valley Branch: Annual General Meeting followed by a Buffet Dance at the Cross Keys Inn, Turnditch, at 7.30 p.m. for 8.00 p.m.

Thursday 12 April

Scottish Section: Annual General Meeting followed by Ladies' Evening. Talk and film on "Old Glasgow" by Ms A. McGrath of the Trefoil Gallery, at the Bruce Hotel, East Kilbride.

Wednesday 18 April

Ontario Section: Annual General Meeting, details to be announced.

Thursday 19 April

London Section: Annual General Meeting at Rubens Hotel, Buckingham Palace Road, London, S.W.1, at 6.30 p.m.

Thames Valley Section: Annual General Meeting followed by a talk on "Local

history" by G. Berry at Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks, commencing at 6.30 p.m. for 7 p.m.

Friday 20 April

Irish Section: Annual General Meeting at the Clarence Hotel, Dublin, commencing at 9.00 p.m.

Manchester Section: Annual General Meeting at the Pavilion Room, Old Trafford, details to be announced.

Midlands Section: Annual General Meeting at the Belfry Hotel, Wishaw, nr. Sutton Coldfield, followed by disco with buffet, details to be announced.

Friday 27 April

Bristol Section: Annual General Meeting at the Royal Hotel, College Green, Bristol, commencing at 7.15 p.m.

"The OCCA"

The annual technical exhibition of the Oil and Colour Chemists' Association (known to many simply as "The OCCA") has become the world's most important event for all those connected with the paint, printing ink, polymer, adhesive, colour and allied manufacturing industries. The OCCA exhibition is held every year in London, England. The symbols for the 1974-79 exhibitions were specially designed by Robert Hamblin, Director and Secretary of the Association's activities attract:



The motif for OCCA-26 used the flags of the enlarged EEC converging on the British flag to symbolise the welcome extended to visitors from overseas to the Exhibitions for more than 25 years. (1974)



The 1974 theme continued at OCCA-27 by showing the world-wide interest aroused by the Association's annual Exhibitions in London which attract visitors from all parts of the globe.



The motif for OCCA-28 emphasised that the target for 1976 was London where all the Exhibitions have been held, and continued the theme of its international aspect.

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Industries

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The Exhibition provides an ideal opportunity for organisations to display and discuss their products and services to a wide spectrum of visitors from all over the world.

Organisations wishing to receive further details should contact the Director & Secretary, Mr R. H. Hamblin, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HAO 2SF, England (Tel: 01-908 1086, Telex: 922670 OCCA G).



The motif for OCCA-31 emphasises the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coalings industries.



The motif for OCCA-30 used the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers.



In 1977 the motif for OCCA-29 used inward pointing arrows to show the many places from which people came to the Exhibition, and these arrows formed outward pointing arrows to show the subsequent spreading of knowledge.

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