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EXPERIMENTAL STATION
RESEARCH AND DEVELOPMENT DIVISION TECHNICAL REPORT
CHEMICALS, DYES AND PIGMENTS DEPARTMENT
E. I. DU PONT DE NEMOURS & COMPANY

DURABILITY TESTING

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ABSTRACT

Durability of TiO_2 pigments is measured by outdoor exposure of paint panels for chalk/fade performance. The testing takes up to 3 years, and new durable pigments are not commercialized until such data is in hand. Accelerated testing in a Weatherometer takes about 3 months, but has been considered unreliable and thought to have little correlation with outdoor results. Accelerated tests have thus been used only to a limited extent for laboratory guidance.

Statistical analyses of more than 1100 paints, however, show a good correlation between outdoor and accelerated chalk/fade data. The accelerated data show larger experimental errors than outdoor results, but this can be compensated for by multiple panels. Accelerated exposures can thus be used to reduce lead time in proceeding with projects for commercialization of new grades and process improvements.

Two supplementary techniques - a UV reactivity test and electronmicroscopy of leached silica shells - were developed for quick lab guidance and to diagnose production problems.

I. INTRODUCTION

As a basis of business decisions and for product development, we should have a precise, accurate and quick test for TiO_2 durability.

Available techniques fall short of these requirements because of:

- intrinsic limitations imposed by the manifestations of "durability",
- experimental difficulties in testing, and
- seeming failure of different durability measures to correlate.

We can:

- detect substantial durability differences
  - •• reliably by outdoor exposure but it takes up to 3 years
  - •• less reliably and in 3 months in the Weatherometer, but considered not to correlate with outdoors.
- measure quickly, characteristics relevant to but not identical with degradation.

We cannot detect minor durability differences reliably and quickly enough for most business needs.

II. OBJECTIVES

The study had three objectives:

- Review the intrinsic limits of chalk/fade testing in the light of current theory,
- Prove or disprove the value of accelerated tests for business decisions, and
- Develop methods for lab guidance.

III. SUMMARY AND CONCLUSIONS

Certain testing problems of "durability" are inherent in its concept, which allows neither its quantitative definition nor its precise measurement.

A comparison of outdoor and accelerated chalk/fade performance ratings of rutile pigments shows:

- Florida and Weatherometer chalk/fade ratings do correlate. Experimental errors of the individual measurements rather than lack of correlation account for most of the data scatter.
- Neither outdoor nor accelerated chalk/fade ratings reproduce well. One-third of all experimental data points differ from "true" by more than ±3.1 and ±4.4 chalk/fade units for Florida and Weatherometer exposures, respectively.
- Accelerated results can be used to shorten lead time for business decisions if experimental and statistical techniques are combined to anticipate exterior performance.

Two supplementary techniques were developed for lab guidance and production assistance:

- A UV reactivity test for quick, precise, though not infallible differentiation of similar pigments, and
- Electron microscopic examination of leached silica shells to pinpoint process failures.

IV. PATENT SITUATION

No filing action is contemplated on the contents of this report.

V. PROGRAM

No further work is contemplated.

VI. PUBLICATION STATUS

Not intended at this time but publication may be considered if it serves Company interests.

VII. SPECIAL SAFETY PRECAUTIONS

Dry white lead was handled exclusively in a hood with greater than usual attention to cleanliness and hygiene. Lead is now handled subject to special OSHA regulations.

UV source and samples are in an opaque box to protect workers.

VIII. ENVIRONMENTAL CONSIDERATIONS

No environmental problems are expected from lab work.

IX. CHEMICALS USED

Titanium dioxide, ammonia, glycerine, white lead, hydrochloric acid, sulfuric acid.

X. TOXICITY DATA

Since 4/1/79 white lead (lead carbonate) is OSHA-regulated with permissible exposure limits of .050 mg/m^3 lead averaged over 8 hrs. and an "Action Level" of .030 mg/m^3.

XI. SPECIAL PRECAUTIONS

None other than safety.

XII. ASSISTED BY

R. W. Blair; Experimental Station Analytical Lab.

XIII. ACKNOWLEDGEMENTS

D. A. Holtzen, CD&P Chestnut Run, suggested the use of lead salts for UV reactivity; H. W. Jacobson helped develop the test. L. A. Wierzbowski provided all exposure data for 1200 paints prepared and evaluated by numerous members of CD&P Department staff.

We thank M. P. Morse, F&F Marshall Lab; V. L. Bacchetta, Engg. Dept. ESD; W. D. Ross for statistical advice and computations; and H. W. Jacobson, P. G. Schmidt, and L. S. Wilkens for useful discussions.

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XV. EXPERIMENTAL AND DISCUSSION

As a basis of business decisions and for product development, we should have a precise, accurate and quick test for TiO_2 durability.

Available techniques fall short of these requirements because of:

- intrinsic limitations imposed by the manifestations of "durability",
- experimental difficulties in testing, and
- seeming failure of different durability measures to correlate.

A. Durability

"Durability" is the continuity of decorative and protective performance of paint films and the effects of their components, for us the pigment, under the influence of weathering. Lack of outdoor durability manifests itself primarily as chalking of the TiO_2 with concomitant erosion, gloss loss and discoloration. Very durable paint films erode without detectable accumulation of chalk.

Considerable progress has been made in understanding chalking and is discussed below in terms of pioneering contributions. Emerging theories define the limits of performance measurements, showing that the degradation process lacks any singular accurate and quantitative definition.

1. Mechanisms of Chalking

A morphological model of chalking was developed and elegantly confirmed by Kaempf et al of Bayer, A. G[1]. They described profoundly variable characteristics of weathered paint films in terms of four combinations:

A. Exposed particles of stabilized TiO_2 resting on and protecting pedestals of photo-active binder (Fig. 1A).

B. Stabilized rutile protecting and degrading photo-inactive binder (Fig. 1B).

C. Holes in a film of photo-active binder degraded directly by UV and catalytically by unstabilized TiO_2 (Fig. 1C).

D. Unstabilized TiO_2 degrading photo-inactive binder.

The authors conclude that "Due to these differences in the surface structure of weathered paint films, the individual test methods used to evaluate weather resistance (measurements of chalking, gloss, weight loss) lead to differing, incomparable results".

FIGURE 1

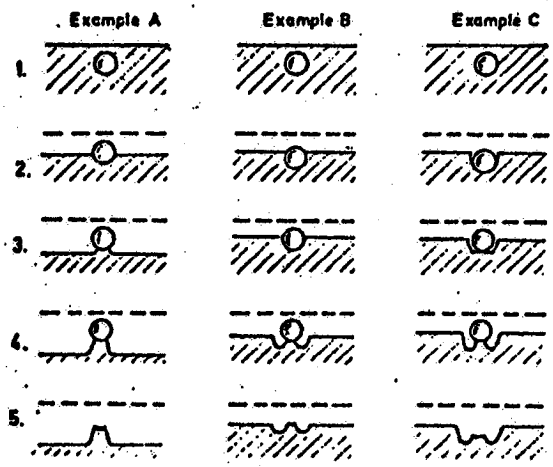


Figure 1—Schematic representation of degradation processes during the weatlfering of TiO_2-pigmented binders. Sample A—Stabilized rutile pigment in binder of low light stability; Sample B—Stabilized rutile pigment in binder of high light stability; Sample C—Unstabilized rutile or anatase pigment in binder of high light stability

FIGURE 1 from G. Kaempf et al
J. Paint Techn. 46 (1974) 57

FIGURE 2

Reflection (Gloss)

Degree of Chalking

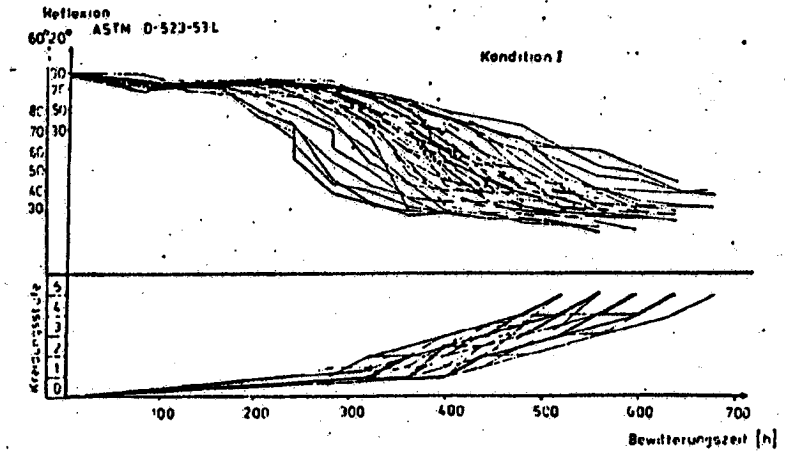


Abb. 2. Glanzverlust und Kreidung aller Versuche im vorgegebenen Versuchszeitraum von 3 Jahren für Kondition I.

Exposure time, hrs.

FIGURE 2 Gloss Loss and Chalking of all Experiments over a Period of 3 Years for Condition I

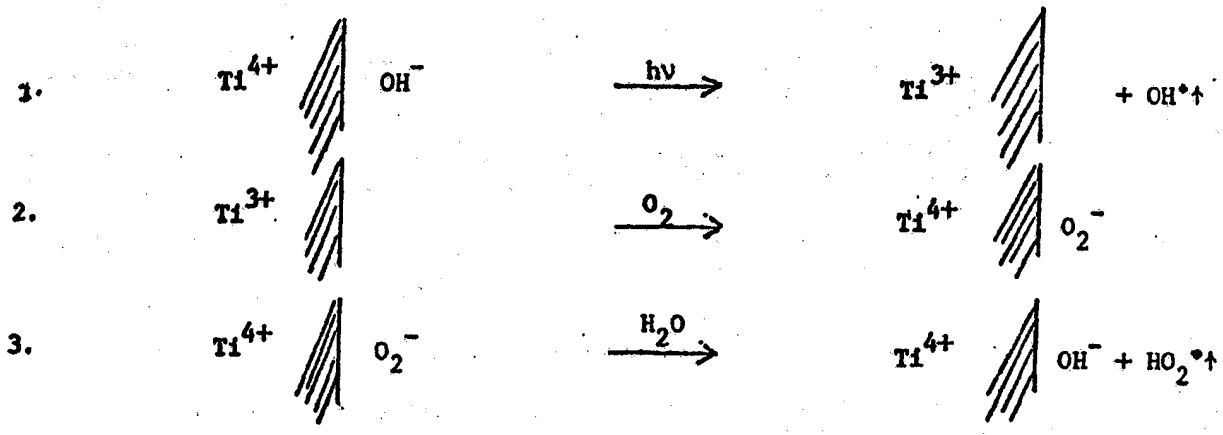
from W. Papenroth et al, DEFAZET 32 (1978) 103

Rate effects of weathering have been studied by Dunderdale et al of LaPorte[2]. They found that pigment volume concentration (PVC) increased during exposure at the paint surface and enhanced the effectiveness of protection by TiO_2.

The degradation sequence of photo-reactive binder has three phases: a period of increasing protection through increasing PVC (decreasing rate of weight loss) is followed by a steady state (constant rate of weight loss) and then by rapidly diminishing protection (increasing rate of weight loss). High PVC improved durability of photo-active binders but diminished durability of photo-inactive vehicle.

2. Chemistry of Chalking

The chemistry of chalking was outlined by Völtz et al of Bayer, A. G.[3] showing UV, water and oxygen to be the essential environmental factors in the TiO_2 catalyzed degradation of binder. The authors detected Ti^{3+}, hydroxyl radicals and peroxides and proposed the following reactions, supported by an abundance of data by numerous other investigators:



The sequence continues 1 - 2 - 3 - 1 - 2...., with an overall reaction:

$$H_2O + O_2 \xrightarrow[h\nu]{TiO_2} OH^{\bullet} + HO_2^{\bullet},$$

and hydroxyl and peroxyl radicals oxidizing and degrading the binder.

The chain of chalking events is cyclic with respect to TiO_2 and can be disrupted at its surface by exclusion of either UV, water or oxygen. Lack of the latter causes photo-graying without significant degradation of vehicle.

Additional details and verifications of TiO_2 solid state and surface involvement in chalking and in particular in photo-graying were provided by Gulley of CR&D[4]. His electron spin resonance and microwave conductivity experiments distinguished readily between rutile and anatase but not among rutiles of different photo-activity. Gulley interprets graying as direct photo-reduction and as a portion of the chalk cycle disrupted by the lack of oxygen.

We can summarize these and many other contributions to the understanding of chalking by a sequence that shows the multiplicity of possible pathways:

1. The absorption of UV radiation by the paint film initiates events. Rates depend on the relative degrees of photo-activity of binder and of TiO_2 stabilization.

    a. In photo-inactive binder, TiO_2 acts as a catalyst for degradation of vehicle. The product of UV radiation acting on TiO_2 is Ti^{3+}.

    b. Photo-active binder is degraded in two ways, directly by UV and catalytically by TiO_2.

    Shielding from UV or passivation of the TiO_2 by coatings or by surface substitution of other ions for Ti can disrupt the degradation sequences.

2. Hydroxylation of TiO_2 is essential to its catalytic effect. UV radiation generates hydroxyl radicals.

3. Water is required for re-hydroxylation. Its lack disrupts or retards the sequence.

4. Oxygen re-oxidizes Ti^{3+} and forms peroxy radicals. Exclusion of oxygen disrupts the sequence and results in photo-graying.

5. Diffusivity of water and oxygen in conventional paint films is involved but rarely rate-limiting.

6. Hydroxyl and peroxy radicals oxidize and degenerate the organic binder.

The general outline of this sequence is well confirmed; details are tentative but not relevant to durability testing. From the foregoing it follows that:

- Intrinsic limitations to testing are imposed by the complexity of events involved, which allows no single nor quantitative statement of performance.

- Experimental problems arise because differences in paint composition, particularly choice of binder and PVC, sensitize different pathways of degradation and affect rates selectively.

B. Exposure Testing

Paints are exposed outdoors to "natural" weathering and "accelerated" in a cabinet that combines high radiation and elevated temperatures with water sprays.

Outdoor exposures are not entirely natural but accelerated by a factor of perhaps 3 over ordinary weathering at the same location by angle and orientation of the panels. Other parameters include choice of location: desert (very high UV, low moisture), tropical (high UV, high moisture), and industrial (low UV, contaminants). Meteorological and seasonal variations add further complications.

"Accelerated" exposures performed in the controlled environment of a laboratory were intended to be more reproducible but are not. Papenroth et al of Bayer[6] reported from an abundance of data - 2 series of more than 150 repeats of identical exposures of a single pigment in one paint formula in 2 Weatherometer arrangements - that "discrepancies of ±50% have to be accepted". Figure 2 illustrates this conclusion by some of their data.

Our pigments were exposure-tested in Florida and sometimes Delaware and in the Weatherometer until the notion arose that Florida and Weatherometer results do not correlate.

1. Precision

The uncertainties of measurement, both outdoors and accelerated, are minimized by the former Pigments Department's instrumented and computerized rating system[7], possibly the most refined one in use. All subsequent conclusions are based on exposures in one paint formula, a blue automotive refinish, Syntex 3833, chalk/fade rated by Daiger and Madson's procedures. According to the authors, this method suffers a 5-point spread for the 95% confidence level in outdoor exposure.

We have evaluated data for both outdoor (Florida) and accelerated (Weatherometer) exposures and find:

Exposure	Standard Deviation of the Test Results for the Same Pigment Exposed in the Same Paint Formula, C/F Units
Florida	3.1
Weather-o-Meter	4.4

Standard deviations (Table I) seem to increase with the chalk/fade ratings, suggesting the use of the coefficient of variation $\left(\frac{\sigma}{\mu}\right)$ in place of the standard deviation (σ) in further computations; but this trend is not firm and we continuedwith σ.

TABLE I

PRECISION OF C/F RATINGS

Same Pigments and Formula,
Different Paintgrinds and Exposure Series

Pigment			C/F Ratings, Standard Deviations and Data Points, C/F Units; n					
			Florida			Weatherometer		
Code	Lot #	Description	Mean	Std. Dev.	Data Points	Mean	Std. Dev.	Data Points
R-900	4083/684	Shipping Std.	9.1	.7	7	8.3	.8	7
"	4479	10 C/F Std. Cand.	15.8	3.9	13	17.3	2.8	11
R-902	4995/674		19.1	2.2	7	17.1	3.2	7
"	4990/673		20.5	.7	2	18.0	1.4	2
"	4995/721		17.0	1.0	3	14.0	3.6	3
"	4926	Shipping Std.	19.7	1.0	3	17.7	.6	3
R-960	3048/661	32 C/F Std.	32.6	3.44	60	26.1	5.16	58
"	6001/694	Shipping Std.	33.0	1.0	3	31.7	1.5	3
CLNC	TC7302	Competitive	21.3	.6	3	*29.7	1.5	3
OR-650	UC7300	Competitive	26.3	1.2	3	*22.7	.6	3
EXPTL.	FX9017A		51.0	5.6	3	*52.7	8.5	3
"	FX9017B		43.3	3.1	3	*53.0	2.6	3
"	FX9022A		33.7	4.2	3	*35.7	3.1	3
"	FX9022B		26.0	1.0	3	*9.3	5.5	3
"	FX9022C		33.3	2.1	3	*31.7	6.1	3
POOLED STANDARD DEVIATION				3.1	119		4.4	115

* F&F Exposure Cycle X-1

Results are based on evaluations of 119 experimental paints rated against 94 paints made up from 2 chalk/fade pigment standards, exposed in 47 series during 1965-1970 both in Florida and in the Atlas Sunshine Carbon Arc Weatherometer, Model XW, with a few F&F Weatherometer cycle X-1 points added.

2. Correlation of Outdoor and Accelerated Exposures

A comparison of outdoor and accelerated chalk/fade performance ratings of rutile pigments revealed:

- Florida and Weatherometer chalk/fade ratings correlate.
- Experimental errors of the individual measurements, rather than lack of correlation, account for most of the data scatter.

This conclusion is based on evaluation of 1,048 experimental paints made up from production samples of most Ti-Pure grades, competitives and experimental pigments, rated against 83 paints from two chalk/fade standards exposed in 50 series during 1965-1970 both in Florida and in the Atlas Sunshine Carbon Arc Weatherometer (Model XW). Included in the analyses were all exposure series 65625-68603 for which matching Weatherometer results were found. These data were not edited.

The correlation is evident from the data plot (Figure 3). The correlation equation

$$(C/F)_{Fla} = .4 + 1.44\ (C/F)_{Acc} - .02\ (C/F)^2_{Acc}$$

accounts for 72% of the data scatter with a residual standard deviation of 5.8 C/F units.

Scatter of 5.4 of these 5.8 C/F units results from the poor precision of the outdoor and accelerated C/F measure, accounting for 86% of the data scatter. Details of the calculation are shown in Table II.

The conclusion that outdoor and accelerated exposure correlate well is consistent with F&F's broad experience but at variance with opinions held in the former Pigments Department:

- F&F experience with accelerated weathering in general can be characterized by the statement that "X-1 cycle predictions of gloss and color retention of coating exposed in Florida at 45°S have been accurate in nearly all instances, where the purpose of the exposure study was to evaluate modifications in the composition of the product... (for example) Comparisons of different pigmentations in a product line"[8].
- "Removed from F&F units because of lack of correlation with Florida exposure" were panels of an exposure series intended to correlate C/F in Florida with 3 F&F accelerated Weatherometer

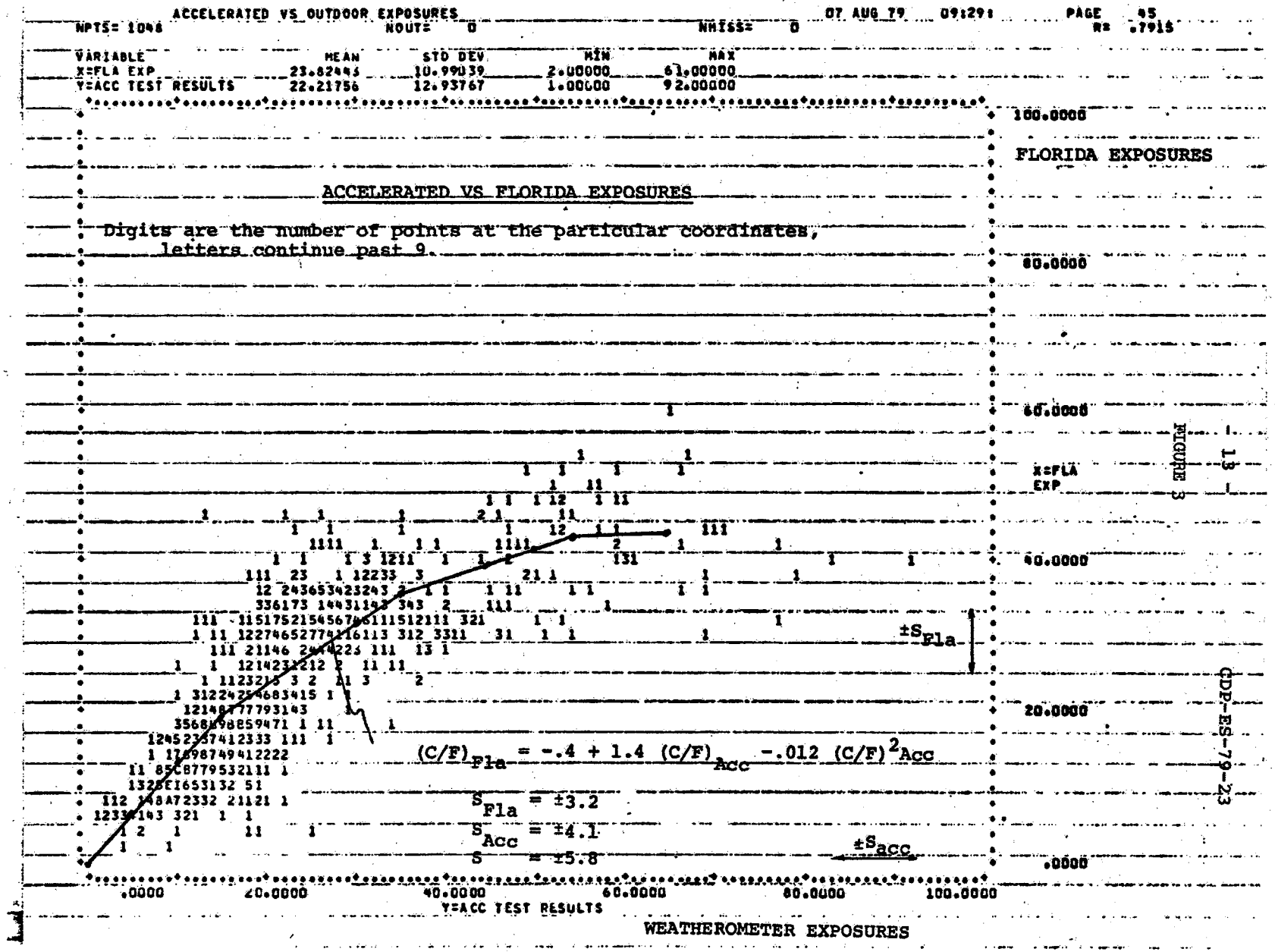


FIGURE 3

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TABLE II

PRECISION OF C/F TESTING

	Standard Deviation, C/F Units
Florida, σ_{Fla}	3.1
Weatherometer, σ_{Acc}	4.4
Correlation Equation, σ_{Cor}	5.8
Accounted Data Scatter, $\sigma_{(Fla, Acc)}$*	5.4
Unaccounted Data Scatter, $\sigma_{Residual}$**	2.2

$$* \ \sigma_{(Fla,\ Acc)} = \sqrt{\sigma^2_{Fla} + \sigma^2_{Acc}}$$

$$** \ \sigma_{Residual} = \sqrt{\sigma^2_{Cor} - (\sigma^2_{Fla} + \sigma^2_{Acc})}$$

These equations are strictly true only for:

$$(C/F)_{Fla} = a + b\ (C/F)_{Acc}$$

and $b = 1$

This condition is approximated in the relevant region of the data (for C/F <40).

cycles[9]. Re-examination of these data does not support this conclusion. F&F exposure cycles X-1 and X-39 correlated quite well with Florida (Figures 4 & 5). Standard deviations calculated from these data agree with the results reported above. F&F cycle X-41 failed to correlate because the C/F standards themselves acted peculiarly, grossly distorting all numerical results.

3. Chalk/Fade Prediction

From these analyses of correlation and experimental precision, we can conclude that Weatherometer data can be used to anticipate outdoor exposure results provided that appropriate statistical techniques and criteria are applied:

- Critical samples must differ by more than 6 C/F units.
- Multiple panels are exposed to make up for lower precision of accelerated results.

An estimate of sample requirements for reliable (95% probability level) differentiation between pigments is given in Table III, based on Students "t" calculations with the standard deviation and correlation equation of Table I and Figure 3.

C. Supplementary Tests

1. UV Reactivity Test

Without hope for a fully satisfactory measure of durability itself, we must guide development work by partial solutions.

Comparisons of rutile and anatase pigments show that the largest performance differences are attributable to the photoavailability of Ti^{3+} sites. We have, therefore, chosen to characterize pigments by photoreactivity rather than hydroxylation.

Discoloration by photo-graying itself[10,11] is slight, ranging from white to light gray. Direct measurements are therefore subject to substantial experimental error.

The addition of lead salts* as both indicator and reactant allows reduction to continue beyond Ti^{3+} and extends the scale to almost black, improving sensitivity of the method to a point where it distinguishes clearly between similar pigments. Representative data are shown in Table IV.

We attribute the darkening to formation of metallic lead from the TiO_2 and UV catalyzed reduction of lead (II) and oxidation of glycerine (Table V).

*Suggested by E. A. Holtzen, CD&P, Marketing Division.

FIGURE 4

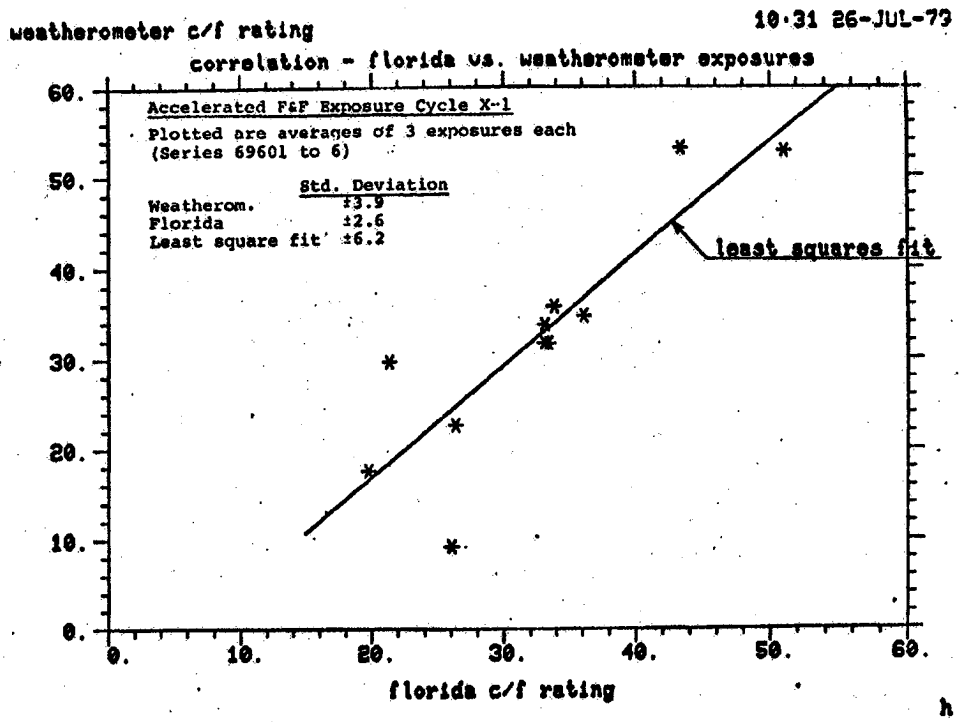

FIGURE 5

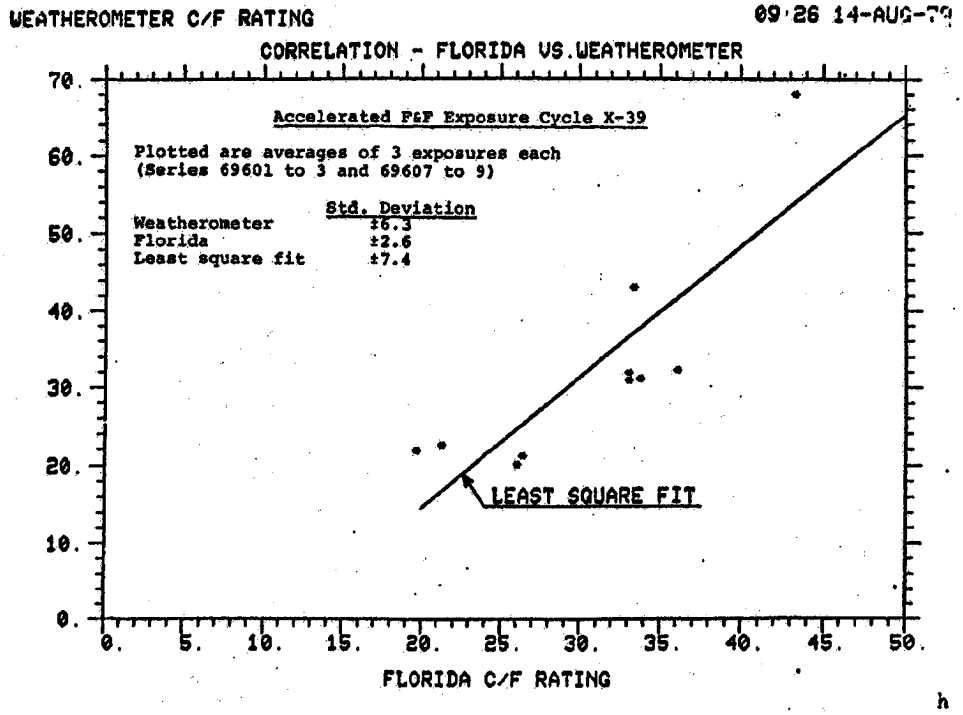

TABLE III

C/F PREDICTION*

If two pigments differ by Δ C/F units..... it takes at least (n+m) exposures** to show that a difference exists with 95% probability of being right.

Δ	At Florida (sec = 3.1)	In Weatherometer (sec = 4.4)	By Anticipation*** (sec = 5.8)
12	2	3	4
10	2	4	6
8	3	5	10
6	5	9	15
5	7	13	
4	10	20	
3	18		

* Based on Students "t" calculation: $\frac{n \times m}{n + m} = \left(\frac{t \times s}{\Delta}\right)^2$ with $t_{95\%,\ 120\ D.F.} = 1.98$

$s = 3.1;\ 4.4;\ 5.8$

** For n "experimentals" plus m "standards", with $n \simeq m$

*** Anticipation of Florida from Weatherometer results

TABLE IV

UV REACTIVITY AND CHALK/FADE

UV Reactivity rated by shades of gray
(Munsell Color Scale):

10 = white - no activity

0 = black - saturation activity

Pigments	Reactivity*	Representative Chalk/Fade Rating
R-960 ShSt. 6098	8.60**	32
R-994 ShSt. 9749	9.2	31
R-931 ShSt. 6791	8.9	28
R-902 ShSt. 9436	7.8	20
R-900 ShSt. 4646	5.00**	10
R-101 Lot 8554	5.1	8
R-100 8939	5.0	
Cyclone Discharge	5.1	

*Standard Deviation $\pm$ .6

**Testing Standards

TABLE V

UV REACTIVITY TEST

PROBABLE CHEMISTRY

$$Ti^{4+} + h\nu \xrightarrow{H_2O} Ti^{3+} + \oplus$$

$$2 \oplus + O^{=} \longrightarrow [O]$$

$$2Ti^{3+} + Pb^{++} \longrightarrow 2Ti^{4+} + Pb^{\circ}$$

$$CH_2\,OH.CHOH.CH_2OH + [O] \longrightarrow \text{oxidation products}$$

On Exposure to Air:

$$2Pb^{\circ} + O_2 \longrightarrow 2Pb^{++} + 2O^{=}$$

Dispersions without glycerine or without TiO_2 stay white. Exposure to air re-oxidizes the lead and bleaches the graying.

The test responds only to the reduction step in the chain of chalking events. As a consequence, the measure should give false negatives by under-rating pigments that derive their protection from a disruption of the hydroxyl involvement in Chalk/Fade. The relative ratings of R-994 and R-960 are probably a case in point. But it is not likely that pigments with an abundance of Ti^{3+} sites are chalk resistant or pigments with few sites are not durable. The test does, therefore, provide valuable but not infallible guidance.

a. Procedure

For testing, .50 g pigment is dispersed with 2.50 g white lead and 1.25 g glycerine. The paste is pressed between 2 microscope cover glasses and exposed for 2 hrs. to UV light (GE bulb H-85A3, UV 85 W) at a distance of 4 inches.

Chips of the most reactive pigments turn almost black; with least reactive TiO_2 they stay nearly white. Graying is rated* against a Munsell scale of neutral grays: 10 White, 0 Black.

Ratings are normalized against 2 standards used in every series: R-960 at 8.60 and R-900 at 5.00. The standard deviation of the test is .6 reactivity units.

Graying response to exposure time, Figure 6, (Table VI) shows that time can be used to optimize results for pigment type. Long exposures enhance differences between stabilized pigments, brief exposures between unstabilized pigments.

b. Applications

The test is sensitive enough to distinguish between similar products. We can even detect the advantage of process modifications.

We tested 3 series of D. P. Fields' sandmilled pigments, and found in agreement with exposure results (Table VII):

- Advantages for sandmilled over control pigments for all grades tested:
  - R-960, R-902 and R-900.

*Instrumental measurement is subject to errors caused by occasional white spots in the chips surrounding small air bubbles.

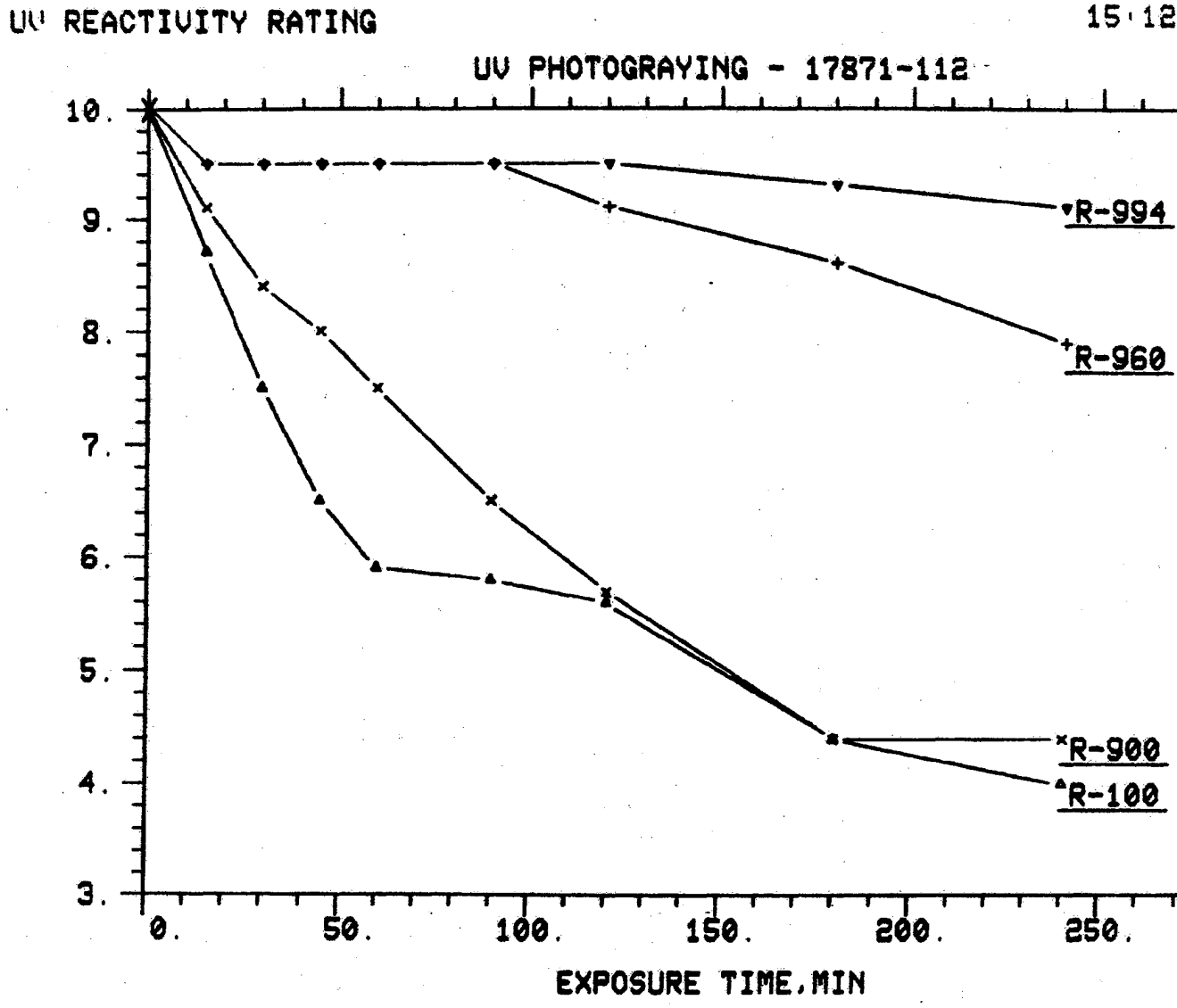

TABLE VI

UV PHOTOGRAYING*

Exposure Time, Min.	R-100 Sh. Std. **	R-900 Sh. Std. **	R-960 Sh. Std. **	R-994 Sh. Std. **
15	8.7 ± .3	9.1 ± .4	9.5 ± .0	9.5 ± .0
30	7.5 ± .5	8.4 ± .7	9.5 ± .0	9.5 ± .0
45	6.5 ± .3	8.0 ± .8	9.5 ± .0	9.5 ± .0
60	5.9 ± .5	7.5 ± 1.0	9.5 ± .0	9.5 ± .0
90	5.8 ± .5	6.5 ± .7	9.5 ± .0	9.5 ± .0
120	5.6 ± .6	5.7 ± .5	9.1 ± .2	9.5 ± .0
180	4.4 ± .4	4.4 ± .4	8.6 ± .4	9.3 ± .3
240	4.0 ± .8	4.4 ± .6	7.9 ± .7	9.1 ± .2

* White 10; Black 0

** Standard Deviation for 1 paste exposed and rated in 5 chips

TABLE VII

SANDMILLED PIGMENTS
UV REACTIVITY

Grade	Code	Type	Micronizer Steam/Pigment	UV Reactivity Normalized to R-960: 8.60 R-900: 5.00		Students "t"**
R-960*	136-A-1	Conventional	1	8.7	8.8±.6 (n = 10)	4.1 > 2.8
	5	"	5	8.9		
	136-B-1	Sandmilled - First	1	9.6	9.6±.4 (m = 20)	$t_{99\%}$=2.8 28DF
	2	"	2	9.6		
	3	"	3	9.7		
	5	"	5	9.4		
R-902	135-A-1	Conventional	1	8.4	8.3±.5 (n = 10)	2.4 > 2.1 $t_{95\%}$=2.1 18DF
	5	"	5	8.2		
	135-B-1	Sandmilled - First	1	9.1	8.9±.6 (m = 10)	
	5	"	5	8.7		
R-900	125-A-1	Conventional	1	4.9	4.8±.5 (n = 10)	2.9 > 2.2 $t_{95\%}$=2.2 14DF
	5	"	5	4.7		
	125-B-1	Sandmilled - First	1	5.2	5.6±.6 (m = 6)	
	5	"	5	6.0		

* Reported previously

** $t = \frac{\bar{X} - \bar{Y}}{s} \sqrt{\frac{n \times m}{n + m}}$

s = standard deviation

n,m = number of exposures of each sample

$\bar{X}, \bar{Y}$ = means

- Effects of micronizing intensity (steam/pigment ratio) on reactivity and, by implication, durability were not detectable, i.e. less than sandmilled versus control or grades versus grades.

Results were analyzed statistically and found better than 99 and 95% probable.

The reactivity test has been used extensively in development efforts for silica-free, durable pigments and zirconia treatments.

2. Silica Shells

A new analytical tool reveals details of the silica shell that imparts durability to R-960.

Aggregation effects, coating integrity, and structural details of Iler coatings are made visible by a transmission electron microscopy of empty silica shells, left behind after the rutile has been leached out by hot concentrated acid[12].

The shape of the shells (Figure 7 A to C) documents aggregation as it existed during silica precipitation. Damage and breakage of shells illustrates effects of micronizing.

a. Procedure

For examination, 50 mg pigment is leached in 10 ml concentrated sulfuric acid at 195°C for 5 hrs. The suspension is centrifuged repeatedly at 5000 rpm, first with concentrated, then with diluted acid, and finally with water. A drop of ammonia solution in the last rinse neutralizes acid residues. Empty shells are kept wet for direct application to TEM grids.

b. Applications

Examination of leached silica shells has been used to show that:

- Glidden's RCL-6 has an Iler silica coating.
- The silica shell of zirconia treated pigments contains some ZrO_2 in its glass structure because it disintegrates in concentrated acid.
- Iler coatings are X-ray amorphous.
- A serendipic R-960 gloss improvement at Johnsonville was related to the state of aggregation or flocculation during the Iler treatment.
- Antimony treatment changes the nature of the pigment surface itself, protecting the particles from acid attack.

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XVII. INDEXING TERMS

Titanium dioxide
Durability
Chalk/Fade
Exposures
Weatherometer
UV Reactivity
Silica Coatings

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