COLORANT-INDUCED EXTERIOR Discoloration of Latex Paints

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Exterior discoloration of latex paint films has been attributed to known causes such as tannin and stain bleeding, mildew and sap staining, color fading and chalking due to certain pigments, and yellowing due to mildewcides and alkyd modification. This paper refers to exterior discoloration of latex paint films containing specific colorant(s). A simple and quick method was adopted to screen paint formulations that may discolor upon exposure to sunlight and water. The exterior discoloration of latex paint films tinted with raw umber colorant is primarily dependent on the manganese oxide(s) present as impurity in the colorant. The role of titanium dioxide in discoloration of raw umber containing latex paint films is also demonstrated. Using this method, the grades of titanium dioxide could be differentiated that facilitate exterior discoloration. A clear correlation was established between the types of surface treatment on titanium dioxide pigment (alumina, zirconia, or silica) versus colorant-dependent discoloration. The investigation demonstrates that the colorant-dependent discoloration is independent of binders, pigment volume concentrations, and mildewcide used in a formulation.

INTRODUCTION

The purpose of this study was to investigate the discoloration of freshly applied latex paint observed in certain regions of the eastern United States. There are several different kinds of discoloration, including yellowing, that can be caused by the presence of certain mildewcides[1] or alkyd modification;[2] fading and chalking which can result from the use of certain pigments and biocides;[3] and the sap staining and tannin bleeding of certain wood substrates.[4] In many cases, the discoloration has been directly or indirectly related to the photoactivity of titanium dioxides. The photooxidative behavior of TiO_2 has been shown to affect binders, pigments, and mildewcides.[5] The studies on this subject have demonstrated that the interaction of ultraviolet radiation with TiO_2 pigments can cause oxygen and water to react and form free radicals that affect binders and result in the chalking of films.[6]

Only a few types of exterior latex paint discoloration other than chalking have been investigated thoroughly. In large part, this has been due to researchers' inability to evaluate pigments quickly and reliably. Up to 10 years ago, there was essentially no viable way to assess pigments at all, a lack that represented a serious barrier to the development of better grades of titanium dioxide.[7,8] Even then, the methods that were developed to explore the photoactivity of TiO_2 required the construction of specialized equipment, which made them impractical for most paint manufacturers and suppliers.

Without analytical tools that are effective and easy to use, it has been difficult to develop information on the roles of specific colorant(s) and TiO_2 in the exterior discoloration of latex paints. The study reported here represented an effort to surmount some of the obstacles impeding an understanding of discoloration. Our goal was two-fold: (1) to develop a method that would facilitate study of the phenomenon and (2) to use that method to gain a better understanding of the factors that cause discolora-

Table 1—All-Acrylic Interior/Exterior Semigloss Formulation

Dispersion	Weight (lb)	Volume (approx. gal)
Propylene glycol	65.0	7.50
Tamol® 165 (21%) dispersant	16.2	1.75
Foamaster VL defoamer	2.0	0.25
Water	58.3	7.00
TiPure® R-706 titanium dioxide	275.0	8.25
Letdown		
Water	25.0	3.00
All-acrylic binder (50%)[a]	489.2	55.50
Texanol® coalescent	24.0	3.00
Water	25.0	3.00
Foamaster VL defoamer	1.0	0.10
Kathon® LX 1.5% preservative[b]	1.7	0.20
Rozone™ 2000 (20%) mildewcide	6.1	0.70
Triton® GR-7M surfactant	2.0	0.25
Acrysol® 2020NPR rheology modifier	28.4	3.18
Acrysol® RM-825 rheology modifier	0.5	0.10
Water	51.8	6.22
Totals	1071.2	100.00

PVC/VS: 24.0%/34.5%
Note: For tinting, 1.25 g colorant/76.0 g paint was used.
(a) All other binders used in this study were substituted on an equal dry volume basis (See *Appendix* 1).
(b) Acrysol®, Kathon®, Rhoplex®, and Rozone® are trademarks of Rohm and Haas Company.

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Table 2—Manganese Oxide(s) Effect on Discoloration

Formulation		ΔE
1.	Paint with only MnO	10.2
	Paint with MnO and Mildewcide	14.0
2.	Paint with natural raw umber, no mildewcide	3.8
	Paint with natural raw umber, mildewcide	4.2
3.	Paint with synthetic raw umber, no mildewcide	<2
	Paint with synthetic raw umber, mildewcide	<2
4.	Paint with Colorants B, C and I[a], mildewcide	0.22

(a) Raw umber color was achieved by mixing Colorant B (Lamp black), Colorant C (yellow oxide) and Colorant I (iron oxide).

The statistical significance of the colorant and mildewcide effects was tested by comparing the ΔE values to the pseudo-replicates obtained by varying PVC levels and biocide. The differences between colorants are highly significant; the mildewcide effect is also significant with greater than 95% confidence (see *Table* A).

Statistical Table A—Effect Tests for Manganese Oxide(s) Effects

Source	Nparm	DF	DFDen	Sum of Squares	F Ratio	Prob > F	
Colorant	4	3	11	50.387034	38.0747	<.0001	LostDFs
Mildewcide	2	1	11	2.940000	6.6648	0.0255	LostDFs
Day and random[a]	4	3	11	2.548179	1.9255	0.1840	Shrunk

(a) Tests on random effects refer to shrunken predictors rather than traditional estimates.

tion. We wanted a simple procedure that would provide a high level of accuracy without a need for special equipment.

MATERIALS AND METHODS

Phase 1

The work in the first phase of the study consisted of determining the simplest and most rapid means of inducing discoloration in susceptible formulations. Since discoloration is a result of exposure to environmental factors, this meant determining the level of exposure to light, moisture, and heat that would produce discoloration in a short time period. To achieve this objective, we exposed typical exterior paint formulations to widely varied combinations of these three environmental conditions for different lengths of time. We evaluated one factor at a time, varying it while holding the others constant.

The materials used in both this and the second part of the study include biocides, binders, colorants, TiO_2, and manganese oxide (*Appendix* 1). The test paints were formulations based on premium all-acrylic binders (*Table* 1). The paints were made with common pigments and colorants at typical use levels. Some formulations employed mildewcides popular in the North American marketplace (see *Appendix* 1); others contained no mildewcide.

All paints were evaluated by casting a 7-mil film on a vinyl scrub chart and allowed to air-dry for five to six hours before exposure. Initial testing was conducted in a temperature regulated greenhouse at 90ºF, equipped with sodium vapor lamps set at 16 hr light and 8 hr dark cycles. The painted samples were cut into 3 × 4 in. pieces and placed in petri dishes lined with moist paper towels and then sealed with paraffin to create a highly humid environment. The whole petri dish set up was then kept in the green house to study the temperature and lighting effects on the paint films for discoloration. For a more realistic assessment, we also placed painted vinyl scrub charts outdoors. To study the effects of intensity of sunlight on films to cause discoloration, the paint surface outdoors was placed by orienting the panels at different positions such as 45º and 90º angles.

Phase 2

On the basis of the results from the first phase of the study, we adopted the following procedure (Sprinkler Exposure Method) for inducing discoloration. After the scrub charts were prepared as described in Phase 1, they were cut in half. One portion was taken outdoors and placed at a 45º or 90º angle face up. Tap water was then misted onto the charts with a Fogg-It™ nozzle at a rate of 0.5 gallon per minute. The misting process ensured that the paint film was completely wet. After two to three hours of exposure, the film was inspected for discoloration. The exposed and unexposed halves of the chart were also scanned separately into a color meter,* and the difference between the color of the two (ΔE) was recorded.

This process was used to evaluate discoloration in a wide variety of paint formulations. The objective in this phase was to identify the roles played by key paint ingredients in discoloration. To achieve this aim, we evaluated the paint components in a standard Rohm and Haas paint formulation (*Table* 1), varying one ingredient at a time while keeping the others constant. To restrict the experimental work to a manageable level, we included only the components traditionally known to be involved in discoloration: binders, TiO_2, colorants, and mildewcides. The influence of pigment volume concentration (PVC) was also investigated. After we had identified manganese (II) oxide as a possible cause for discoloration, we included it in our testing at experimental levels of 1,000 ppm.

RESULTS

Phase 1

The first part of the study clearly indicated that a combination of direct sunlight and a completely wet film was necessary for discoloration to occur. In the early part of this testing, we conducted exposures in environments with varying levels of relative humidity, but the body of the paint itself was not wet. With these paints, we saw discoloration only where moisture had condensed on the film. Interestingly, temperature level had no significant effect on the development of discoloration; testing conducted during the summer months of July and August produced no more discoloration than trials performed in the cooler fall months of October and November.

Phase 2

The results from the second part of the study were extremely noteworthy as they revealed a previously unsuspected source of discoloration—raw

*UltraScan XE from Hunter Lab, with instrument setting at CIE L*A*B* (CIELAB 10º/c).

umber pigments—and also provided new understanding of the role played by titanium dioxide pigments in this phenomenon.

The first clue to raw umber's influence was a very strong correlation between the presence of some of these colorants and discoloration (*Table* 2). The one puzzling aspect of this discovery was the fact that discoloration occurred only with natural raw umber colorants. When a raw umber color formed by mixing such colorants as lamp black, yellow oxide, and brown iron oxide was employed, the paints did not show any color changes. A more detailed analysis of the raw umber pigments in the study suggested an explanation; the natural umber pigments contained manganese oxide not present in any of the other umber colorants. By the process of elimination, the manganese compound had to be the source of the color changes.

This conjecture was confirmed by formulating a paint with manganese oxide and no colorant and using the Sprinkler Exposure Method to treat it (*Table* 2). The result was the greatest degree of discoloration observed in this testing. Where formulations containing natural raw umber pigment demonstrated a color change (ΔE) of approximately 4 units, the paint containing manganese oxide showed a ΔE of >10 units. Contrast these figures with those for the other raw umber colorants, none of which showed ΔE values as great as 2. These data clearly demonstrated manganese oxide to be the primary cause of discoloration in the formulations tested.

Significantly, although natural raw umber proved to be a primary source of discoloration, the nature of the TiO_2 in the formulation greatly affected the extent of the color change (*Table* 3). With modern titanium dioxide products, surface treatments are used to enhance certain properties (e.g., gloss and durability) of the pigment by changing its reactivity. Typical surface treatments include alumina, alumina/zirconium, alumina/silica, and alumina/zirconium/silica. This trial indicated that the type of surface treatment and degree of discoloration were linked. Generally, the alumina-only and alumina/zirconium treatments used in low- and medium-durability grades were associated with a greater degree of discoloration than any of the treatments employing silica.

Interestingly, while the titanium dioxide's surface treatment had a major impact on discoloration, other variables thought to be important in this respect—binders (*Table* 4), biocides (*Table* 5), and PVC (*Table* 6)—had little or no effect.

In our binder testing, we prepared a variety of paints according to our standard formula. Every paint had the same raw umber pigment but with one of four different binders. For each of the test binders, there was a version with a low-durability TiO_2 and one with high-durability TiO_2 (*Table* 4).

Parenthetically, we should note that the variations in the ΔE values for the low durability grade TiO_2 versions are somewhat misleading in that they appear to show that the binder *can* influence the degree of discoloration. Our testing does not support that conclusion. In an effort to understand the ΔE differences, we conducted several tests on a paint with the same binder and low-durability TiO_2 combination over several days. Somewhat surprisingly, the ΔE values differed by as much as two to three full points. The reason for these differences is not yet clear; they may be due to variations in the ultraviolet radiation on the days tested. Whatever the explanation, it is clear that the absolute ΔE values for different binders from tests performed on different days cannot be compared.

At any rate, the point worth noting in these studies is that, in all instances, the formulation containing the low-durability TiO_2 discolored badly, but the paint with the durable grade had a much lower ΔE. From this, we can conclude the silica-based surface treatments somehow inhibit the reactions that result in color changes. These findings underscore the importance of using a high-durability grade of TiO_2 when formulating with natural raw umber pigments.

Table 3—Titanium Dioxide Effect on Discoloration

No.	Titanium Dioxide Grades[a]	Surface Treatment(s)	ΔE
	Source A		
1.	Low durable w/biocide	Al	5.5
2.	Medium durable w/o biocide	Al	3.3
3.	Medium durable w/biocide	Al	3.8
4.	High durable w/biocide	Al, Si	2.5
	Source B		
5.	Low durable w/o biocide	Al	3.6
6.	Low durable w/biocide	Al	4.3
7.	Moderate durable w/biocide	Al, Si	2.6
8.	High durable w/biocide	Al, Si	2.0
	Source C		
9.	Medium durable w/o biocide	Al, Zr	4.5
10.	Medium durable w/biocide	Al, Zr	4.9
11.	High durable w/biocide	Al, Si	1.5
	Source D		
12.	High durable w/o biocide	Al, Si, Zr	2.4
13.	High durable w/biocide	Al, Si, Zr	2.1

(a) See *Appendix* I for details.

The durability and surface treatment effects are highly significant (p-value < .01) but source and biocide are not significant effects. However, the power for detecting source effects is only 15%, and the power for detecting biocide effects is only 30%, based on the design of the study. Even if source or biocide had an effect, it would probably not have been detected in this study (see *Table* B).

Table B—Effect Tests for Titanium Dioxide Study

Source	Nparm	DF	DFDen	Sum of Squares	F Ratio	Prob > F	
Source	4	2	11	0.2051420	0.8203	0.4655	LostDFs
Durability	3	2	11	1.9300311	7.7174	0.0080	LostDFs
Biocide	2	1	11	0.3089655	2.4709	0.1443	LostDFs
Surf	4	2	11	2.5552516	10.2174	0.0031	LostDFs
Day and random[a]	6	5	11	2.8642605	4.5812	0.0167	Shrunk

(a) Tests on random effects refer to shrunken predictors rather than traditional estimates.

Biocides had equally little effect on raw-umber-related discoloration (*Table* 6). This may be surprising to some as mildewcides such as chlorothalonil and iodopropargyl butyl carbamate (IPBC) are known for their film-chalking and yellowing properties. The point is that these tendencies are related to another phenomenon and not to the presence of manganese oxide. This was demonstrated by the fact that the control formulation containing no biocide showed a significant ΔE.

The PVC ratio also proved to have no measurable impact on discoloration (*Table* 6). We tested a variety of paints made with acrylic emulsions with PVC levels ranging from 20 to 70%. In no case was there any significant difference in the degree of discoloration.

Because the experiments were conducted in stages and results from one experiment led us to investigate other parameters, a formal statistical design was not used in these studies. Hence, standard methods of testing the significance of these effects could not be applied. However, an ad hoc test is constructed by treating ΔE results for negligible effects (PVC level and biocide) as pseudo-replicates. Since biocide had little effect on discoloration results, the ΔE values for different biocides can be used to construct a worst-case estimate of variability; that is, treating any biocide effects as if they were only noise, the standard deviation of the ΔE's for the five biocides and control can be used as a conservative estimate of noise variation for a single day. The standard deviation estimated in this way for biocides data is 0.441 ΔE units, with five degrees of freedom.

Similarly, PVC level had little effect on discoloration results. The ΔE values for different PVC levels can also be used to construct a worst-case estimate of variability for panels exposed on a single day. Six different paints were made, following the same formula but with different PVC levels. All six paints were exposed on the same day. The standard deviation estimated in this way for PVC effects is 0.259 ΔE units, with six degrees of freedom. The two estimates are consistent within the confidence intervals for the variance estimates. Because PVC levels and biocides were tested on different days, these two studies also give us a single-degree-of-freedom estimate of day-to-day variability. This is a weak estimate, however it does provide a means of testing effects from different exposure days. The statistical significance thus obtained from the ΔE values from various studies in this investigation is provided as a footnote under respective tables.

DISCUSSION

The discoloration or yellowing of latex or alkyd paints has been investigated by many scientists in the past.[1-3] As far as the yellowing related to IPBC mildewcides is concerned, some investigators believe the process begins with the photolysis of the iodo group and proceeds with the formation of cumulene, a yellowish material.[1]

None of the articles in the scientific literature, however, has reported the phenomenon discussed in this paper. Unlike the well-documented yellowing that occurs for a variety of reasons, we have found that a yellow-brown discoloration can occur when a specific colorant, natural raw umber, is exposed to light and water in the presence of less durable titanium dioxide. Raw umber is a mixture of naturally mined iron oxide, often from different sources, and synthetic iron oxides designed to meet definite color, composition, and physical specifications.[11] The natural iron oxide ores are known to contain manganese dioxide at a level of 6 to 25%.[11] Given the role that manganese oxide has been shown to play, it is clear that the degree of discoloration in raw umber-tinted paint films can vary considerably, depending upon the process and purity level of the iron oxide.

The extent of the discoloration that occurs also depends on the nature of the titanium dioxide. The absorption of ultraviolet wavelengths by TiO_2 in the presence of water results in the development of free radicals and hydrogen peroxide.[5] To improve the exterior durability of TiO_2, the producers have attempted to reduce the destructive effects of ultraviolet light on the pigment by various means of surface treatments.[3] Some of the surface treatments used are alumina coatings; alumina and silica treatments to boost exterior durability to withstand chalking and gloss resistance; and alumina, silica, and zirconia treatments to compound and protect the pigments from other factors that affect exterior durability. Based on the properties improved, the titanium dioxide pigments are sold in different grades—low durable, medium durable, and high durable.[12-14] The data produced by this study clearly show that, in paints formulated with manganese-containing colorants, it is critical for formulators to employ one of the more durable TiO_2 grades in order to minimize discoloration.

Two other simple laboratory test methods reported previously also depend on the principles of catalytic activity. The method described by Irick[15] is based on the oxidation of isopropynol to acetone by ultraviolet light in the presence of TiO_2. He showed that this reaction was proceeded by a free radical mechanism and that oxygen was re-

Table 4—Binder Effect on Discoloration

Binders[a]	ΔE[b] Values Low Durable (Al treated)	High Durable (A1, dense Si Treated)
A	2.67	0.77
B	3.67	1.07
C	5.6	0.35
D	2.76	0.35

(a) See Appendix for details.
(b) Data compiled from several experiments conducted on different days.

The TiO_2 durability effect is highly significant (p-value < 0.0001), but the binder effect is not significant compared to the estimated day-to-day variation. The power for detecting the binder effect is only 15% because of the design of the study; this means that even if there is a binder effect, there is only a 15% chance of detecting it using this experiment design.

Table C—Effect Tests for Binder Study

Source	Npar, m	D, F	DFDe, n	Sum of Squares	F Ratio	Prob > F	
Durability	2	1	10	18.483200	54.3427	<.0001	LostDFs
Binder	4	3	10	0.743422	0.7286	0.5580	LostDFs
Day and Random[a]	6	5	10	2.649181	1.5578	0.2573	Shrunk

(a) Tests on Random effects refer to shrunken predictors rather than traditional estimates.

Table 5—Biocide Effect on Discoloration (Formulations with Raw Umber)

Biocide[a]	ΔE[b] (1.25% Raw Umber)
No Biocide	4.1
Biocide A	3.2
Biocide B	3.8
Biocide D	4.0
Biocide E	3.0
Biocide F	3.7

(a) See *Appendix* 1 for details of the biocides tested.
(b) The standard deviation of the ΔE's for the five biocides and control can be used as a conservative estimate of noise variation for a single day. The standard deviation estimated in this way is 0.441 ΔE units, with 5 degrees of freedom.

Table 6—Effect of PVC Level Effect on Discoloration

PVC Levels	ΔE
Standard Fail Control (24%)	2.59
20	2.79
30	2.92
40	3.04
50	2.58
60	2.48
70	2.30

PVC level had little effect on discoloration results. The ΔE values for different PVC levels can also be used to construct a worst-case estimate of variability for panels exposed on a single day. Six different paints were made, following the same formula but with different PVC levels. All six paints were exposed on the same day. The standard deviation estimated is 0.259 ΔE units, with 6 degrees of freedom. This estimates the variation for days plus reformulation. The two estimates are consistent within the confidence intervals for the variance estimates.

quired. Later, Brownbridge[8] demonstrated, using this method, that the rate of acetone formation was proportional to the accelerated weathering performance of a group of titanium dioxide pigments. He showed that the photocatalytic activity values determined from this reaction correlate well with the 24-month Florida exposure results for a large number of commercial and experimental titanium dioxide pigments.

In 1990, Braun[9] described a method in which titanium dioxide, lead salt, and oxidizable organic medium were combined to create a black paste. The reduction of lead salt "counts" redox cycles through the accumulation of black metallic lead that darkens the initially white paste. The difference between the starting white color and the ultimate darker color is measured by reflectance. The test method developed and reported in this paper is somewhat similar to the catalytic activity method described by Braun, with the difference that the color-changing metal is manganese as opposed to lead. The precise mechanism of the manganese reaction has not been examined in our work. However, it appears that the manganese (which exists in several oxidation states in nature, ranging from +2 to +7) does undergo oxidation/reduction cycles in response to oxidizing agents such as hydrogen peroxide and switches states from +2 to +4 and vice versa. The +4 oxidation state of the element is largely found in manganese dioxide and is reported to be brown in color.

SUMMARY

This work demonstrates a phenomenon not previously recorded in the scientific literature: the role of natural raw umber in contributing to exterior latex paint film discoloration. The discoloration is caused by manganese oxide occurring as contaminant in the natural iron oxide used to make raw umber. The study shows that photooxidative degradation of titanium dioxide contributes to this phenomenon. The raw-umber-dependent discoloration of latex paint films can be greatly reduced by substituting a more durable (dense silica-treated) grade of titanium dioxide for a less durable (treated with alumina only) grade in a paint formulation. This work also shows that in paints containing raw umber (natural), the "yellowing" or discoloration occurring upon exposure to light and water (rain) is often not related to the nature of the mildewcide or binder.

A simple test method described in the paper allows one to screen formulations quickly for these types of discoloration without having to invest in time and expensive apparatus or equipment. The test can be completed in less than a day and thus provides a tool that allows paint companies and pigment manufacturers to quickly predict the weathering behavior of products in their programs.

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Appendix 1

Additive/Type	Product Name	Manufacturer
Colorants:		
Raw umber	Colorant L	Creanova Inc.
Black	Colorant B (lamp black)	Creanova Inc.
Yellow	Colorant C (yellow oxide)	Creanova Inc.
Brown	Colorant I (brown iron oxide)	Creanova Inc.
Raw umber	Colorant L	Color Corp. of America
Mildewcides:		
Chlorothalonil	Nuocide® 404D	Creanova Inc.
Iodopropargyl butyl carbamate (IPCB)	Polyphase® P-20-T	Troy Chemical Company
n-Octyl isothiazolones (ITA)	Skane® M8; Rozone™ 2000	Rohm and Haas Company
ITA/carbendazim/diuron blend	Mergal® S89	Troy Chemical Company
Binders:		
Acrylic binders	Rhoplex® AC-2508 Rhoplex®	Rohm and Haas Company
	SG-10 Rhoplex® ML-200	Rohm and Haas Company
	UCAR® 626	Union Carbide Corp.
	Acronal® 6183	BASF Corp.

Titanium dioxide (TiO_2)[3]

Type[a]	Surface Treatment	Product Name	Manufacturer
Low durable	Al	Tiona® RCS-9	Millennium Inorganic Chemicals
		TiPure® R-900	DuPont Chemical Company
Medium durable	Al, Si	Tiona® RCS-2	Millennium Inorganic Chemicals
		TiPure® R-942	DuPont Chemical Company
High durable	Al, Si	TiPure® R-706, TiPure R-960,	DuPont Chemical Company
		CR® -826	Kerr-McGee Chemical Corp.
Medium durable	Al, Org	CR® -828	Kerr-McGee Chemical Corp.
		Tiona® RCS-535	Millennium Inorganic Chemicals
High durable	Al, Zr, Org	Kronos® -4310	Kronos, Inc.

(a) Low and High durability described with respect to chalk resistance and gloss retention.[4]