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Research Report

GLOSS RETENTION OF V54 ESTERS

I. PIGMENTATIONS WITH RED LEAD

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ABSTRACT

V54 enamels retain their low application viscosity for several hours after application, and show pronounced pigment settling in the drying film with several pigments. This produces an unusually thick clear layer over a pigmented layer of V54 enamel. The thicker the clear layer, the more time it takes to erode this layer, and the better the gloss retention of these enamels on outdoor exposure. Cuprous Oxide and Red Lead showed extreme settling. Chrome Yellow, Molybdate Orange and Ferrite Yellow show less severe settling in V54 enamels.

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LIST OF ABBREVIATIONS

V54-Alcohol	= 2-vinyl 1,3-dioxolane 4-butanol
V54-OP	= Ester of orthophthalic acid and V54 alcohol
V54-I	= Ester of itaconic acid and V54 alcohol
V54-ICM	= Blend of esters of itaconic, citraconic and mesaconic acids and V54-alcohol
V54-enamels	= Enamels with the above mentioned esters as major binder material. The esters used contained approximately 80% bis-ester and 20% mono-ester (mol.-%).

GLOSS RETENTION OF V54 ESTERS - I PIGMENTATIONS WITH RED LEAD

INTRODUCTION:

Work on the development of V54 Maintenance Primers led to the discovery that the gloss retention on outdoor exposure of V54 finishes pigmented with red lead was markedly better than the gloss retention of most common pigmentations of V54 enamels.

OBJECTIVES:

Determine the cause of the markedly better gloss retention shown by red lead pigmented V54 finishes and reduce the findings to a principle generally applicable to V54 enamels.

RESULTS AND CONCLUSIONS:

It was found that the good gloss retention shown by red lead pigmented V54 enamels is due to severe settling of this pigment during the curing stage of the paint film. Pigment settling results in an unusually thick clear layer on top of the pigmented layer. The longer time required to erode a thick layer than to erode a thin layer is the cause of the observed improved gloss retention.

There is no apparent chemical effect or interaction of red lead with V54 esters that provides improved gloss retention.

The severe settling of some pigments in films of V54 enamels is a paint deficiency which causes flooding and poor reproducibility in color. Therefore, pigment settling as shown by red lead and some other pigments cannot be used as a means for improving the gloss retention on exposure of V54 enamels.

Cu_2O (W-416) showed pronounced settling and improved gloss retention to an even greater degree than red lead. This is probably due to the fact that Cu_2O is a severe drying inhibitor for V54 esters and keeps the film wet for over two days. The prolonged time that W-416 pigmented films remain at spray viscosity allow more complete settling of the pigment or formation of a thicker clear layer on top than in the case of red lead. Chrome Yellow (W-679) Molybdate Orange (W-622) and Ferrite Yellow (W-630) showed pigment settling and improved gloss retention to a much lesser extent than red lead.

Flooding in V54 enamels, resulting from using pigments with poor dispersion characteristics, can be reduced or overcome by accelerating the set-up speed through addition of drying accelerators or polymeric materials.

We found again that the bottom side (interfacial with the substrate while curing) of V54 enamels is much more durable than the top surface. The difference is greatest for V54-I and smallest (not very significant) for V54-ICM, or V54-OP. At the moment we have no way to use this knowledge for improving the out-doors performance of V54 enamels.

PATENT STATUS:

No patent action is being considered at the present time.

ACTION PROPOSED:

This work is being closed out with the publication of this report.

PUBLICATIONS:

No publications are proposed.

ACKNOWLEDGEMENTS:

I gratefully acknowledge the stimulating discussions with J. H. Lowell and W. T. M. Johnson. The alertness of M. J. Cabry, Jr., who performed most of the laboratory work, contributed to the results.

DISCUSSION:

Introduction:

W. M. Duffy, while developing V54 maintenance primers, found that several primers pigmented with red lead, showed better gloss retention on exposure, than was usually observed in high gloss V54 enamels, formulated as automotive topcoats.

These primers were formulated as medium or low gloss paints. For more valid comparison with other formulations red lead containing V54 enamels were formulated as high gloss topcoats. Exposure results of these enamels confirmed the original observation. During the first six months of Florida exposure the red lead pigmented enamels retained their gloss significantly better than other pigmentations (e.g. TiO_2) of V54 enamels.

It was hoped that knowledge of the cause of this effect would lead to a principle which could be applied to improve the outdoor durability of all V54 ester topcoats.

The Chemical Nature of Red Lead

Originally it was assumed that a chemical mechanism caused the improved gloss retention of red lead pigmented V54-ester enamels. In order to determine which particular aspect of red lead was the major cause, the chemical properties of red lead were investigated as different variables. The variables were studied as follows:

1. The element: lead as a film protecting element.

The following lead containing pigments and U. V. absorbers were exposed:

Leaded Zinc Oxide (W-18)

Chrome Yellow (W-679)

Molybdate Orange (W-622)

Lead Silico Chromate (KW-5781)

Lead salicylate (Normasal, a U. V. absorber from National Lead)

Basic Lead phosphite (Dyphos, a U. V. absorber from National Lead)

The leaded zinc oxide, lead silico-chromate, lead salicylate and basic lead phosphite did not significantly improve the gloss retention of V54 enamels, compared to the regular TiO_2 (W-50) pigmented enamels. Only Chrome Yellow (W-679) and Molybdate Orange (W-622) pigmented enamels showed slightly improved gloss retention.

2. Red lead as metal oxide was compared with Cu_2O, Cr_2O_3, ZnO, HgO and Fe_2O_3.

The only outstanding performer was Cuprous Oxide (W-416), which showed extremely good gloss retention, even better than red lead pigmented enamels. It also caused more severe flooding than red lead, probably due to the fact that cuprous oxide severely retards the dry (by more than two days) thus having more time to settle completely to the bottom of the film.

Fe_2O_3 (W-630) pigmented enamels showed slightly improved gloss retention (compared with W-50 pigmentations) but it also showed slight flooding, equal in degree to Chrome Yellow (W-679) and Molybdate Orange (W-622).

3. The importance of the valency of lead in read lead was studied by comparing litharge (PbO) and PbO_2 with red lead (Pb_3O_4). Both the PbO and PbO_2 pigmented films performed very poorly on exposure (Table I).

4. The basicity of red lead was examined by comparing basic lead carbonate ($2PbCO_3.Pb(OH)_2$), lead borate (approx. $Pb(BO_2).H_2O$; 70.5%Pb) and lead sulfate ($PbSO_4$).

All three compounds performed very poorly on exposure.

From these results we concluded that none of the isolated aspects of the chemical nature of red lead was the exclusive cause of the improvement in gloss retention of V54-enamels pigmented with red lead.

Interaction between Red Lead and Binder

1. V54-esters

It was considered possible that red lead on storage with V54-esters reacted with the esters to form a more durable binder. Therefore red lead was ground in V54-esters by 47-process. The mill bases were stored for two weeks and the red lead was separated (by centrifuging) from the V54-esters. The resulting binder materials were formulated into clear and W-50 (TiO_2) pigmented finishes (10% SBO-alkyd resin on binder, P/B 50/100).

The red lead treated esters showed very similar infrared absorption spectra and equal gloss retention on exposure as the untreated esters. This indicated that the V54 esters did not react on storage with red lead.

2. Conventional Binders

The improved gloss retention of red lead pigmented films seemed to be confined exclusively to formulations containing V54-esters as the major binder material. Red lead pigmented finishes formulated with alkyd resins (in the automotive refinish 93-Line), with nitrocellulose (in the automotive 253-Line) and with PMMA (in the automotive 885-Line) did not show any beneficial effect of red lead (Table II). The alkyd and nitrocellulose formulations showed the poor color-fastness of red lead without any improvement in gloss retention, and the PMMA formulation showed the excellent durability characteristics of the "Lucite"* automotive topcoats.

Concentration of Red Lead

In order to determine the correlation between the concentration of red lead and the improvement in gloss retention, red lead containing V54 enamels were exposed in two different types of ladders:

1. One series contained red lead as single pigment over a range of pigment volume concentrations.

2. Another series was formulated as a pigment blend of rutile TiO_2 (W-50) and red lead (W-349) at a constant total pigment volume. (The W-50 concentration increased with decreasing W-349 concentration.)

These ladders showed that (1) the single pigment enamels returned equal gloss retention throughout the entire ladder, independent of the red lead concentration (Table III). This gloss retention was of the same order as the gloss retention of clear V54-ester films. (2) Films pigmented with blends of W-50 and W-349 showed the gloss retention of TiO_2 pigmented enamels, without any beneficial effect of the red lead present in the film (Table IV)

These results indicated that (1) the presence of red lead was not essential to obtain improved gloss retention, and (2) that addition of red lead to other pigments would not lead to generally improved gloss retention.

*Registered Du Pont Trademark

Flooding of Red Lead

During the preparation of enamels pigmented with W-50 and W-349 a remarkable phenomenon was observed. Horizontally dried paint films showed a striking color difference between the top side and the bottom side of the film. The top side with only a very slight orange color had essentially the color of TiO_2 and the bottom side had the color of red lead. This was caused by pigment settling, as was evidenced by the fact that when the film was dried in a normal horizontal position the red lead color gravitated toward the substrate, whereas when it was dried in an inverted position (with the paint film downward) the color migrated to the surface of the film. The chemical nature of the substrate (glass, aluminum foil, automotive dip primer 64-1690 over bonderized steel) had no influence on this phenomenon.

Single pigment enamels pigmented with red lead also showed a striking color difference between top and bottom surfaces. The bottom had a darker color than the top, indicating pigment separation along the lines of particle size.

The important variables for the degree of color difference between top and bottom were the initial viscosity of the enamel and the set-up speed. Formulations with V54-OP (3.6 poises) showed less difference between top and bottom than formulations with V54-I (0.8 poises). The color differences between top and bottom were smaller in formulations with 10% PMMA (setting up faster) than in formulations with 10% air-drying alkyd, which stayed longer at spray viscosity.

Lack of any indication of the existence of a chemical mechanism and the demonstration of severe settling of red lead in the curing paint film led us to investigate pigment settling as a possible cause of the improved gloss retention. It was postulated that severely settling pigments, such as red lead, impart better gloss retention to V54 enamels because of the formation of a thicker layer of clear film over the pigment. This thick layer of clear simply lasts longer before being eroded away than the thinner layer of clear over non-settling pigments. Chalking or bronzing starts when the bare pigment particles are exposed on top of the paint film.

The more rapid increase of viscosity after spraying of conventional finishes prevents the pigments from settling. This explains why red lead does not cause improved gloss retention in conventional finishes.

Gloss Retention of the Interfacial Surface of V54 Enamels

To establish the validity of the postulated thick clear layer as cause of the improved gloss retention, we compared the gloss retention of the normal top surface of films of red lead pigmented V54 enamels with the bottom surface (originally in contact with the substrate but removed and inverted). If the top surface were to have improved gloss retention due to a thicker clear layer the bottom (interfacial) surface should have poorer gloss retention, due to a thinner clear layer.

The exposure results were contrary to expectations. The bottom surfaces (initially in contact with the substrate) showed better gloss retention than the normal top surfaces. It had been shown previously that there is a difference in the chemical nature of V54 ester films at the top surface as compared with the bottom surface.

By removing films and exposing them upside down it was shown that the bottom surface is more gloss-retentive than the top surface, regardless of pigmentation. This chemical effect apparently overrides the opposing effect of pigment settling (and the resulting thinner clear layer) on the gloss retention of the film, even in the red lead pigmented films. At this moment we have no way to obtain "bottom durability" throughout the entire film.

Upward versus Downward Dried Films

In order to eliminate the differences in binder material between top and bottom surfaces, red lead pigmented V54 enamels were dried in two different ways:

1. Horizontally with the paint film upward (normal position).

2. Horizontally with the paint film downward (upside down).

The upside-down films were not ideally suited for comparative exposure studies, because the red lead had sunk so deep to (or through) the film surface that these films had lower initial gloss than the upward dried films. The difference in gloss between "upward" and "downward" films was greater for V54-I (0.9 poises) than for V54-OP (3.7 poises). After two months exposure in Florida the downward dried films, with the lead concentrated on the surface, showed severe loss of gloss, chalking and discoloration of the red lead (Table VI). The films dried in normal position and having a thick clear layer over the pigmented layer, still had the attractive appearance of the new films. This proves that red lead by itself does

not improve the gloss retention of V54 esters, and although the actual thickness of the clear layer over pigments was not measured, the combined data provide sufficient evidence that the outstanding gloss retention is due only to the thick clear layer over the pigmented layer. The homogeneous erosion of V54 esters (no checking) results in the maintenance of good appearance throughout the clear film life time, especially with V54-I (which shows less dirt collection than V54-OP or V54-ICM).

Other Pigments

Red lead is not the only pigment which shows settling combined with improved gloss retention of V54 enamels.

Cuprous Oxide (Cu_2O, W-416) shows both phenomena to an even greater extent than red lead. The fact that W-416 is a severe drying inhibitor for V54 esters and kept the films wet for over two days, thus allowing more complete settling of the pigment, may be the reason for the magnitude of this effect. Chrome Yellow (W-679), Molybdate Orange (W-622) and Ferrite Yellow (W-630) also showed considerable pigment settling and improved gloss retention, but to a much lesser degree than red lead.

Pigment settling and flooding can be eliminated by formulating V54 products with fast set-up; e.g. through addition of drying accelerators such as benzoyl peroxide or t-butyl hydroperoxide or through addition of polymers such as PMMA or CAB. The addition of polymers also improves the pigment dispersion stability in the liquid state.

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EXPOSURE STUDIES USED FOR THE DATA IN THIS REPORT

#17882	Top versus Bottom of V54 Enamels
#18082	Colored Pigments in V54 Enamels-V
#18412	Red Lead in V54 Enamels-I
#18541	U.V. Absorbers in V54 Enamels
#18563	Red Lead in V54 Enamels-II

TABLE I

DIFFERENT LEAD OXIDES

GLOSS RETENTION ON FLORIDA EXPOSURE

Binder: V54-ICM/PMMA 100/10

10.7% Pigment Volume.

	60° GLOSS			
	Initial	2 Months	4 Months	6 Months
PbO	56	8	9	6
Pb_3O_4	90	56	41	31
PbO_2	88	30	9	12

TABLE II

RED LEAD IN DIFFERENT BINDERS

GLOSS RETENTION ON FLORIDA EXPOSURE

	20° GLOSS			
	Initial	2 Months	4 Months	6 Months
V54-I	78	57	25	15
V54-OP	91	28	25	9
V54-ICM	84	25	11	6
"Duco"*	73	4	1	1
"Dulux"**	48	18	6	1
"Lucite"***	91	32	41	37

* Formulated in the automotive 253-Line
** Formulated in the automotive refinish 93-Line
*** Formulated in the automotive 885-Line

TABLE III

DIFFERENT CONCENTRATIONS OF RED LEAD IN V54-ICM/PMMA 100/10 (SINGLE PIGMENT FORMULATIONS)

Concentration of Red Lead (P/B, wt. ratio)	FLORIDA EXPOSURE 60°Gloss				20°Gloss			
	Initial	2 Mo.	4 Mo.	6 Mo.	Initial	2 Mo.	4 Mo.	6 Mo.
90/100	82	52	41	31	84	25	11	6
30/100	92	61	49	28	78	29	16	5
10/100	90	70	60	34	89	31	28	9
3/100	90	69	57	31	86	41	25	8

TABLE IV

DIFFERENT CONCENTRATIONS OF RED LEAD IN RED LEAD/TiO_2 PIGMENTED ENAMELS WITH CONSTANT PIGMENT VOLUME (11% PVC)

Weight Ratio Red Lead/TiO_2	FLORIDA EXPOSURE 60°Gloss			20°Gloss		
	Initial	2 Mo.	4 Mo.	Initial	2 Mo.	4 Mo.
90/5.3	83	21	16	60	4	3
30/33.3	88	36	21	78	8	3
10/37	87	23	16	75	4	2
3/46.8	85	23	16	77	4	2
0/50	70	29	22	64	4	2

TABLE V

TOP VERSUS BOTTOM

OF RED LEAD PIGMENTED ENAMELS

GLOSS RETENTION ON FLORIDA EXPOSURE

	60° Gloss			
	Initial	2 Mo.	4 Mo.	6 Mo.
V54-I Top Surface	90	80	62	49
V54-I Bottom Surface	85	74	72	70
V54-OP Top Surface	92	61	56	41
V54-OP Bottom Surface	86	58	63	56
V54-ICM Top Surface	90	56	41	31
V54-ICM Bottom Surface	87	61	65	40

TABLE VI

RED LEAD ENAMELS, DRIED UPWARD VS. DRIED DOWNWARD

GLOSS RETENTION ON FLORIDA EXPOSURE

	60°Gloss	
	Initial	2 Months
V54-I Dried Upward	99	87
V54-I Dried Downward	20	1
V54-OP Dried Upward	100	57
V54-OP Dried Downward	91	18