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Report No. R-68-9

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Research Report

EMULSION PAINT RESEARCH - IV

Date Issued	:	February 8, 1968
Period Covered	:	6/67 - 1/68
Project No.	:	P-13226
Previous Reports	:	R-64-33, R-65-22, R-65-112, R-66-59, R-66-126, R-67-54
Notebook Nos.	:	8986, 9115

ABSTRACT

The problems of obtaining better flow and appearance in dripless flat paints of the "Lucite®" Wall Paint type are discussed. Leads are given for improving the leveling and hiding power and for decreasing cost but with a sacrifice in driplessness. Flat emulsion house paints based on the emulsions used in "Lucite" Interior and Exterior Enamels (IO-4 & IO-3) have better leveling and appearance. However, these failed worse than #50 "Lucite" House Paint when exposed over a badly flaked old paint substrate.

Higher gloss and improved water resistance have been obtained for IO-3 Acrylic Emulsion Paints. These dry sufficiently hard for taping in about 4 hours at room temperature.

Nonionic surfactants of the Triton type which differ only in chain length have vastly different effects on viscosity, driplessness, leveling, spackle cracking and stability to ions.

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1/31/68

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EMULSION PAINT RESEARCH

INTRODUCTION:

In previous reports (Ref. 1, 2, 3) techniques were described for improving the leveling and lapping of semi-gloss emulsion paints. The recently commercialized Lucite® Interior Enamels were the first products to use these new techniques.

In the present report attempts are described to extend the new formulating approach to our most important consumer paints - "Lucite" House Paint & "Lucite" Wall and Ceiling Paints.

Also included are descriptions of the following research

(1) Improving the leveling of dripless paints
(2) Decreasing cracking over spackle
(3) Increasing the hiding power
(4) Increasing the coalescence and hardness of high gloss emulsion paints
(5) The role played by nonionic surfactants in thickening, stability and adsorption.

OBJECTIVES:

The goals are to develop information on important emulsion paint phenomena and to see that the information is used to improve existing products and to design new products.

SUMMARY AND CONCLUSIONS:

Wall Paints

Leads are desirable for a new generation of "Lucite" Wall Paints which will maintain the advertised features of driplessness, ease of application, etc., but which will have improved flow and appearance. The problem is that for driplessness we need a pseudoplastic paint with appreciable yield value and a high viscosity at low shear rates. These properties are the opposite of those required for good leveling, absence of brushmarks, roller patterns, etc.

An experimental dripless paint which showed improved leveling when brushed was formulated. It was based on a higher viscosity modification of IO-3* thickened with the Veegum montmorillonite clay used in 392-Line "Lucite" paints. The formulation is impractical in that it does not level when rolled and its viscosity increases on the shelf. Its viscosity is higher than "Lucite" except at the low shear rates that control leveling. Its viscosity at 0.1 $sec.^{-1}$ decreases from 800 to 400 poise when the measurement is made after first shearing at 529 $sec.^{-1}$.

*IO-3 =MMA/2EHA/MAA emulsion = 47.5/49.5/3

Apparently the shear under the brush but not under the roller is sufficient to reduce the viscosity and allow surface tension forces to cause flow and leveling.

There are at least 3 types of important dripping. Blobs of paint drop from a brush dipped into the can, paint runs down the handle of a brush especially when ceilings are painted, and splatters of paint are flicked off a brush or roller during application. The rheology required to prevent each type of dripping seems to be different.

If we achieve improved leveling by formulating a paint whose yield value and viscosity at low shear rates are lowered by shearing during use, it will probably run down the handle of the brush to a greater extent than present "Lucite".

An improved balance between good leveling, splatter resistance and low cost is possible with high can consistency paints (110 Krebs Units) based on IO-4* and Thickener LN. Cost can be reduced still further by using a lower cost, harder, royalty-free iminated acrylic emulsion (RC-B-91484) methylmethacrylate/2-ethylhexylacrylate/methacrylic acid = 60/36/4 with a low cost external plasticizer. The advantages of this type of paint over "Lucite" Wall Paints are lower cost, improved appearance, reduced cracking and peeling. The rheology is similar to that of the new emulsion semi-gloss paints i. e., higher viscosity at intermediate shear rates, lower viscosities at very low and very high shear rates and lower yield value than "Lucite" Wall Paints.

The dry hiding power can be increased and the hiding power loss on drying can be decreased in "Lucite" Ceiling White by adding extender to increase the pigment volume concentration or by replacing the present "Ti-Pure®" R-901 with new, still experimental TiO_2's from Pigment Department.

<u>House Paints</u>

Flat emulsion house paints have been formulated with much better leveling and slightly better build than #50 "Lucite" House Paint. When these were compared with #50 for durability over cracked old oil paint, they were superior on the weatherometer but inferior when exposed 45° South in Delaware in December, 1966. A house paint based on IO-4 and a small amount of Thickener LN cracked worse than those based on IO-3** or IO*** which contained five times as much Thickener LN. Additional exposures have been made of the softer IO-3 emulsion in formulations containing both propyleneglycol and ethyleneglycol monoethyl ether for improved coalescence and adhesion.

*IO-4 = iminated MMA/2EHA/MAA=48/48/4
**IO-3 = " " " " =47.5/49/5/3
*** IO= " " " " =45/53/2

Gloss Emulsion Paints

High gloss acrylic emulsion paints which should have good durability even when dried at low temperatures have been formulated from IO-3 with Amberlac 165 added for hardness and early tapeability. Propyleneglycol or diethyleneglycol monobutyl ether greatly improve the water resistance of these paints probably because of improved coalescence.

Nonionic Surfactants

Nonionic surfactants differing only in chain length have vastly different effects on viscosity, leveling, spackle cracking and ionic stability. The amount adsorbed on emulsion particles has been determined.

ACTION TAKEN OR PROPOSED:

We have proposed that the composition of #50 "Lucite" House Paint, which is durable enough according to Marketing (Ref. 14) be changed as little as possible to obtain better leveling and slightly better build. The smallest changes which give these properties involve adjusting the monomer ratio from the present 45/53/2 (MMA/2EHA/MAA) to 45/52/3 and replacing methylcellulose with Thickener LN. Two 4 gallon batches of paint with this composition were made and given to W. D. Deveise and W. J. Starr for exposure testing.

Suggestions in the form of Backlog Proposals (#67-10 and Ref. 15) have been made for studying "Penetration of Emulsion Paints in Porous Surfaces" and "Improving our Patent Position in Emulsions".

We propose to continue this project with emphasis on learning how to improve the texture of "Lucite" Wall Paint without sacrificing driplessness.

G. C. Bell under his Distributive Project will evaluate methods for measuring low shear rate viscosity and yield stress immediately after shearing. He also plans to determine how the rheology of a paint affects the so-called brush-drag, the cushion and the applied film thickness.

PATENT STATUS:

Status of Prior Proposals

No office action has been received on FFD-1240 (Water Base Paints having improved leveling and lapping.) The present plan is to refile as FFD-1240A, when an office action on FFD-1240 is received to cover the additional classes of thickeners mentioned in M. J. McDowell to C. E. DeBoer 9/22/66.

Patent Proposal FFD-1253 which covers Mesirov's brush-drag compositions containing polyethyleneimine has been filed mainly because of Elchem's interest in polyethyleneimine-modified vinyl acetate copolymer paints.

The following are the imination patent proposals and their corresponding U.S.P. numbers -

FFD-3006A	U.S. 3,261,796 (Dow have initiated an interference on this patent).
FFD-1218A	U.S. 3,309,331
FFD-1222	U.S. 3,261,797
FFD-3046	U.S. 3,261,799
FFD-2048A	The patent office has indicated that the 13 claims will be allowed.
FFD-1834	Formerly F970A covers iminated carboxylic acrylic <u>solution</u> copolymers and adhesive compositions.

FFD-1192 Acrylic copolymer Latex Paint Modified with Benzophenone has issued as U.S. 3,320,198.

New Proposals

Refiling FFD-1240 to cover paints containing new classes of thickeners has been proposed .

FFD-1821 proposed claiming "Treatment of High Acid Number Oil Modified Alkyd Resins with an Aziridine Compound". This proposal which has electrodeposition implications was forwarded to Legal on 2/8/67.

Competitive Patents

Two patents on thickeners U.S. 3,301,829 and U.S. 3,306,863 have issued assigned to General Aniline and Geigy Chemical Corp. respectively. U.S. 3,301,829 claims

18. "A composition comprising a water-soluble partial ester of:
    (1) a micelle-forming hydroxyl-containing non-ionic surface active agent selected from the group consisting of alkylene oxide condensation products with an active hydrogen-containing hydrophobe, alkylolamine condensation products with fatty acids, alkylolamine condensation products with fatty esters, and glycol and polyesters of fatty acids and

(2) an alkali-soluble interpolymer of an ethylenically unsaturated carboxylic acid anhydride with a terminal ethylenically unsaturated copolymerizable monomer selected from the group consisting of vinyl ethers, vinyl esters and -olefins, said partial ester containing from about 0.1% to about 3% of the carboxyl groups as ester groups."

20. "A composition as defined in claim 18 wherein the surface active agent is an alkyl phenol-ethylene oxide condensate and the interpolymer is a vinyl methyl ether-maleic anhydride interpolymer."

We concur with C. E. Bartsch that Claim 20 "appears to rather specifically cover compounds of the Thickener L type."

General Aniline informed us they would sell Gantrez AN-119 and include in the purchase price a royalty for a non-exclusive license to manufacture partial ester compositions under U.S. 3,301,829 (See M. J. McD. to J. W. B. 7/7/67). On 11/21/67 we requested (ref. 18) General Aniline to provide information on the amount of royalty and whether an unlimited license was available. No reply has been received yet.

The U.S. 3,306,863 patent assigned to Geigy claims ethylene/maleic anhydride/Triton X-100 thickeners and discloses the use of styrene/maleic anhydride based thickener which are superior to Thickener LN (ref. 19, 3, 20). Use in latex paint and pastes for textiles is disclosed. Advantages claimed are improved color value, better wash fastness, improved cracking resistance, lower solids, improved hand, etc.

U.S. 3,291,930 assigned to Koppers claims thickeners for latices based on styrene/maleic acid esterified with small amounts (1-5%) of the polyethylene ethers of monohydric aliphatic alcohols. These were prepared in the dry state or in toluene.

U.S. 3,290,416 (12/6/66) assigned to Pittsburgh Plate Glass is directed to solution acrylic polymers modified with propyleneimine and "could be recognized as dominating IO latex." However it appears that we have a basis for ignoring this patent in view of our prior sale of iminated copolymer adhesives. Also the pending application FFD-1834 (Usala) has an earlier priority date. PPG attorneys indicated that they intended to file a disclaimer with regard to Claims 4,5,7,15 and 16 in U.S. 3,290,416 because of F. & F.'s prior commercial activity. Our iminated emulsions are included among several commercial products on which Legal will render an infringement opinion. Crosslicensing may result.

Our soft acrylic emulsions stabilized at high pH with non-ionic surfactant, and 0.5-3.3% methacrylic acid are considered by Legal Dept. to be subject to royalty under Rohm & Haas' U.S. 2,795,564. The royalty amounts to about $100,000/year and the patent runs till 1974. No royalty is due on IO-4 (RC-11011) or RC-11199 because they contain more than 3.3% acid.

The patent situation for "Polymer Latices and Aqueous Dispersion Paints" has been summarized in a 71 page report by C. E. Bartsch.

PUBLICATION STATUS:

This research should not be published until effective patents are obtained.

ACKNOWLEDGEMENTS:

Specific references are made in the text to many who have contributed with suggestions, information or samples.

DISCUSSION:

The principal defect of most emulsion paints is poor apparent hiding power. It is not always due to low opacity or loss of opacity on drying (Ref. 2). It often results from spreading the paint too thinly and poor leveling. (See Appendix 1)

Requirements for Improved Leveling

There is now evidence that the following paint properties result in improvements in leveling -

(1) Lower viscosity at low shear rates especially after shearing,

(2) Lower yield stress in the paint especially after shearing,

(3) Slower increase in viscosity and yield stress during the initial drying period,

(4) Thicker films,

(5) Higher surface tension,

(6) Narrower striations or furrows due to brushing or rolling.

Dripless paints especially the "Lucite" type recover their "gel" structure and driplessness very quickly. This and their high viscosity at low shear rates, and fairly high yield values explain their poor leveling.

We need data on the changes in yield value and low shear rate viscosity immediately after shearing at high shear rates. The difficulty is that our rotational viscometers require such a long time to register a steady reading (at the very low rpm's used for low shear rate measurements) that fast changes in the structure of dripless paints cannot be measured yet.

Dr. Patton (Ref. 4) has derived an equation which predicts that for Newtonian liquids the time (t) required for a given degree of leveling to occur is given by $t = 0.036\,\lambda^4 \log \frac{Zo}{Zt} \frac{N}{SX^3}$ where λ = distance between the bottoms of the brushmark furrows Zo & Z_t = half the depth of the brushmarks at time zero and time t respectively

N = viscosity (at the appropriate shear rate if the paint is non-Newtonian)

S= surface tension

X= film thickness

G. G. Bell (Ref. 6) and O. Lin (Ref. 7) have shown or predicted that leveling is also increased by higher shrinkage stresses or longer relaxation times respectively.

Importance of Yield Stress

If paints have a yield stress they will not flow unless the stress developed by surface tension is greater than the yield stress. The maximum stress that can be produced by surface tension can be estimated from the following equation (Ref. 4)

$$\text{Maximum Stress} = 248\ \frac{S\ \ Z\ \ X}{\lambda^3}$$

The maximum stress that would be developed if a paint had a surface tension of 25 dynes/cm., a striation depth of 1 mil (= 0.0026 cm = 2Z), a wet film thickness of 2 mils (0.0051 cm.) and a brushmark wavelength of 0.15 cms. is

$$\text{Maximum Stress} = \frac{248 \times 25 \times .0013 \times .0051}{0.15^3}$$

$$= 13\ \text{dynes/cm}^2.$$

A stress of 13 dynes/cm.^{2} would not be sufficient to initiate flow of "Lucite" Wall Paint since batches of dripless paint have a yield stress much higher than 13 dynes/cm^2, e.g., batch P-730905 of 392-429 had a yield stress of 95 dynes/cm.^{2}, batch 760040 of 392-429 was found by G. G. Bell to have yield stresses of 68 dynes/cm.^{2} by test method TD-508N, 49 dynes/cm.^{2} after prior shearing at 529 sec.$^{-1}$, and 100 dynes/cm^2 by Beeferman and Bergren's method (Ref. 9).

There is a possibility that paints could be formulated to have sufficient yield stress when undisturbed and unsheared to minimize dripping, but insufficient yield stress immediately after brushing and rolling to prevent leveling.

The present test method for measuring yield stress (TD-508-N) involves waiting 2 3/4 minutes after first shearing for 15 seconds. During this time "Lucite" Wall Paint has undoubtedly regained some of its gel structure which may have been temporarily destroyed by shearing under the brush.

G. G. Bell is studying the possibility of modifying the test method to enable yield stresses to be measured, immediately after shearing so that we can measure the break-down of the gel structure by rolling or brushing.

The viscosity of emulsion paints which are pseudoplastic varies from 1000 poises to 0.5 poise depending on whether the measurements are made at shear rates characteristics of leveling (o.1 sec.$^{-1}$) or at shear rates characteristic of brushing (20000 sec.$^{-1}$). If the paint is thixotropic the viscosity will also vary with the length of time it has been sheared or with the time it has been at rest since last subjected to shearing stresses.

One way to estimate thixotropy is to measure the area enclosed by a hysteresis loop. Figures 1 and 2 obtained by G. C. Bell for "Lucite" Ceiling White 392-429 and an experimental IO-3 flat paint (8986-159B) respectively suggest that the former paint is not very thixotropic as the up and down curves are not very different.

Experimental Paints with Improved Leveling

An experimental dripless emulsion paint (8986-159B) containing Veegum and methylcellulose and formulated from a modification of IO-3 (in which 80% of the methacrylic acid was added in the last 45% of the mixed monomers gave a bigger hysteresis loop (Fig. 2) and leveled quite well after brushing.

These hysteresis loops might be more instructive if they could be obtained over a wider range of shear rates and especially at the very low shear rates encountered in leveling. Unfortunately our viscometers when used at these low shear rates and r.p.m.'s require several minutes to show a constant reading. The apparent viscosity reading for "Lucite" Ceiling White (at the shear rates important in leveling) actually increases with time of shearing. At o.1 sec.$^{-1}$ shear rate 392-429 gives the following apparent viscosities on the Haake Rotoviscometer -

APPARENT VISCOSITY FOR 392-429 (POISES AT 0.1 SEC.$^{-1}$)	SECONDS ELAPSED SINCE SHEARING BEGUN
850	50
1510	100
1550	150
1580	200

An increase in viscosity with time of shearing is typical of rheopectic and not thixotropic systems. Apparently the scale readings on the Rotoviscometer at low shear rates respond too slowly to follow any breakdown in the gel structure.

A possible explanation for the improved leveling of the aforementioned 8986-159B paint is that its viscosity at low shear rates especially after shearing at 529 sec.$^{-1}$ is much less than that of "Lucite" Ceiling White.

This is illustrated by the following data:

APPARENT EQUILLIBRIUM VISCOSITY AT 0.1 SEC.$^{-1}$

	Fresh Paint Sample	Paint Sample Previously Sheared Vigorously
Control of "Lucite" Ceiling White 392-429	1600 poises	1600 poises
Experimental IO-3/ Veegum Paint 8986-159B	800 poises	400 poises

The above experimental paint is higher in viscosity at higher shear rates, e.g. 3 poises at 529 sec.$^{-1}$ vs. 2 poises for "Lucite" Ceiling White.

Although this experimental paint leveled much better than the control when both were applied by brush, there was no significant improvement in leveling or appearance for rolled films. The reason for this may be that the shearing rates and shearing stresses developed during roll application are much lower than during brushing. Another explanation for poorer leveling in general for roller applied paints is that the leveling forces due to surface tension would be weaker because of the greater distance apart of the peaks and valleys. The greater spacing between the peaks would be analogous to using a brush which caused widely spaced striations i.e., a larger and therefore a smaller stress from the equation on page 8. The wet film thickness was lower for roller application than for brush application and this too would decrease leveling.

Other formulations of dripless emulsion paints based on this modified IO-3 emulsion and Veegum were compared for leveling, viscosity and yield stress. The effects of Rohm & Haas' Acrysol ASE-60 acrylic thickener, their Triton X-405 nonionic surfactant and Dow's methylcellulose thickener on viscosity and leveling were investigated because these are the additives which control the rheology of "Lucite" Wall Paints. Although differences are apparent in the data on the next page on viscosity and yield stress no improvement in leveling was observed. Methylcellulose was very detrimental to leveling. Thickener LN caused a large increase in viscosity initially but unfortunately the viscosity continued increasing on aging in these Veegum-containing paints.

EFFECT OF ADDITIVES ON RHEOLOGY OF VEEGUM-CONTAINING DRIPLESS PAINTS

Emulsion	% Acrysol ASE-60	% Triton X-405	Viscosity at 0.1 sec.$^{-1}$ Fresh Sample (Poise)	Viscosity at 0.1 sec.$^{-1}$ Sample Sheared at 529 sec.$^{-1}$ (Poise)	Yield Stress (dynes/cm^2) TD-508N	Leveling
IO-3	0	0	520	450	39	Poor
"	0	0.5	2240	1700	87	"
"	0.07	0	700	280	69	"
"	0.07	0.5	1400	1080	83	"
HG* & Piccopale	0	0	1200	2000	35	"
" "	0	0.25	1700	2000	63	"
" "	0.07	0	1400	2400	61	"
" "	0.07	0.25	2100	2600	67	"

*For this experiment the usual Triton X-405 poststabilizer was omitted from the HG emulsion and added to the final paint (where indicated).

When the imination of the IO-3 emulsion was omitted both the emulsion and the paint were considerably more viscous and less stable on the shelf.

Veegum-containing paints based on IO or IO-3 (RC-11013 type) were too low in viscosity until methylcellulose or Thickener LN was added. These thickened paints showed poor leveling.

IO-4 paints containing Veegum even when applied by brush showed poor leveling when thickened with methylcellulose. Improved leveling after brushing but not after rolling was obtained for an IO-4/Thickener LN paint pigmented with a base formulated by John Gallager. This experimental base contained Veegum and the other pigments used in White "Lucite" Paint but the usual dispersing agents were replaced by E. R. Werners' water dilutable itaconic acid copolymer. (Ref. 21). This paint bodied excessively on the shelf and caused much worse cracking than 392-429 when both were applied with a 20 mil clearance doctor blade over calcimine.

Non Dripless but Splatter-Resistant, High Consistency Wall Paints With Improved Leveling

The recent commercialization of 394-Line "Lucite" Interior Enamels has given consumers possibly for the first time very high consistency paints (Stormer Viscosity - 100-120 Krebs Units) which show good leveling. The paints are not dripless because their yield stresses are zero or at least so low we cannot measure them. Their high can consistency is advantageous for increasing paint pick-up and for decreasing settling and splatter.

If purchasers of these semi-gloss paints like the application properties as much as did the panelists in the series of tests preceding commercialization, it would be worthwhile to consider the desirability of marketing similar flat paints with improved leveling and appearance.

There are many consumers who dislike the dripless variety of paints. Many even prefer to use our 2nd Line (-the much lower ingredient cost, less scrubbable Flowkote® Wall Paint) simply because of its smoother texture. If these consumers are numerous enough perhaps we should give them high consistency paints which apply easily to give uniform appearance in one coat. The chances of succeeding will be increased if the paint:

(1) has good opacity when dry
(2) shows an increase in opacity on drying
(3) spplies easier in a thick film than in a thin film
(4) shows a minimum of brushmarks, roller stipples, skips or lapmarks
(5) is more splatter-resistant than "Lucite" Wall Paint

Some progress towards these goals will be described later.

Emphasis has been placed also on low mill cost. Low mill cost necessitates using as many as possible of the following approaches.

(1) low solids
(2) high pigment volume concentrations

(3) large amounts of low cost extenders which give plenty of pigment/air interfaces for "dry-flat hiding"
(4) reduced amounts of titanium dioxide
(5) emulsions now being manufactured in Fort Madison and used in sufficient quantity to justify bulk handling and storage
(6) minimum amounts of relatively high cost additives such as thickeners, glycols
(7) low cost diluents for the emulsion such as Piccopale emulsion now used in "Lucite" Wall Paints or low cost plasticizers
(8) acrylic emulsions containing more methylmethacrylate and less 2-ethylhexyl acrylate
(9) royalty-free acrylic emulsions such as RC-11011 or RC-11199

Selection of Emulsion

We have concentrated on acrylic emulsions because of their

(1) ease of manufacture
(2) wide formulating latitude
(3) good acceptance by consumers partly as a result of our effective advertising of the "Lucite" trade-mark
(4) good stability when shaded with F. & F.'s colorants

There may, however, be an incentive to switch from acrylics to Elchem's Elvace® vinyl acetate/ethylene emulsions. Dr. R. B. Holmes is currently studying this important question.

Selection of Acrylic Emulsion

We selected copolymers of the IO-4 type because

(1) at the usual pH's of our paints and especially in the presence of Triton X-100 they become very viscous and therefore require less expensive thickener at the desired low solids

(2) they show good lapping and leveling in the presence of thickeners derived from high molecular weight maleic anhydride copolymers and non-ionic surfactants.

(3) they usually give freeze-thaw stable paints even when small amounts of glycols or additional surfactants are added.

(4) No royalty is payable to Rohm & Haas since they contain significantly more than 2.5% acid.

Effect of MMA/2EHA/MAA Ratio on Second Order Transition Temperature

The following table shows the approximate Tg's for various ratios:

	MMA	2-EHA	MAA	Tg in °C
	100	0	0	105
	0	100	0	-55
	0	0	100	150
HG	44	54	2	-2
IO	45	53	2	0
"Softer" IO-3	45	52	3	1
IO-3	47.5	49.5	3	5
"Old" IO-4	45	51	4	3
Present IO-4	48	48	4	7
RC-B-91484	60	36	4	27
9115-132	76	20	4	58

The Tg's were calculated for the terpolymers from the values shown for the homopolymers neglecting the effect of imination.

A high Tg makes the paint harder, more difficult to coalesce.

Use of Plasticizer

A high Tg allows the use of more low cost plasticizer in interior paints if plasticizer migration and embrittlement are only minor problems. Hydrocarbon and styrene-butadiene emulsions which embrittle and small amounts of dibutyl phthalate have been used previously without problems in "Lucite" Wall Paints.

The following table shows the need for about 20 parts of benzylbutyl phthalate/100 parts of binder solids in order to obtain scrubability of 50% pigment volume concentration paints based on the RC-B-91484 emulsion (ratio 60/36/4).

EFFECT OF PLASTICIZER ON SCRUB RESISTANCE OF 50% PVC EMULSION PAINTS BASED ON MMA/2EHA/MAA=60/36/4

	Parts of Benzyl-butyl phthalate	Scrub Resistance with 1/2% Ivory Flakes* Film aged 1 day for almost instantly	Appearance of paint Film after 1000 cycles with 5% Bon Ami (Film aged 1 week)
CONTROLS			
9115-32	20	OK for 1000 cycles	slight erosion
9115-33A	10	Failed at 125 cycles	slight erosion
9115-33	0	almost instantly	complete erosion (failed at 15 cycles)
392-429=HG	-	OK for 1000 cycles	slight erosion
Lucite® **	-		
392-529=BP		OK for 1000 cycles	" "
"Lucite"			

* TD-530
** PVC - 45%

Additional tests showed that good scrubability could be obtained with the following emulsions provided the levels shown below of benzyl butyl phthalate were used:

MMA/2 EHA/MAA	PARTS OF BENZYLBUTYL PHTHALATE REQUIRED (PER 84 PARTS OF POLYMER SOLIDS) FOR GOOD SCRUB RESISTANCE
45/51/4	0
48/48/4	0
60/36/4	20
76/20/4	40

All the paints formulated from the above emulsions using the BP type pigmentation (titanium dioxide/diatomaceous earth) and Thickener LN showed very good leveling.

Improved Opacity

In flat wall paints it is easy to achieve excellent dry hiding power by increasing the pigment volume concentration to such a high level that there is insufficient emulsion polymer to occupy the voids left between the pigment particles by the evaporation of water. These minute voids and the large pigment/air interfaces scatter light. When the PVC is high enough there is so much of this type of scattering that the usual loss of hiding power on drying* can be eliminated.

The following table shows that there is a loss of hiding power on drying at 50 and 55% PVC, no significant difference between the wet and dry hiding power at 60% PVC, and a definite increase in hiding power at 75% PVC. The higher PVC's were obtained by replacing some of the IO-4 solids with the aluminum silicate extender (W-189) used in "Lucite" Interior Enamels.

*The five reasons for losing hiding power on drying are discussed in Ref. 8.

EFFECT OF PIGMENT VOLUME CONCENTRATION ON HIDING POWER OF IO-4 EMULSION PAINTS

Emulsion	IO-4	IO-4	IO-4	IO-4	IO-4	Control HG+ Piccopale in 392-429
Pigment Volume Concentration%	50	55	60	65	75	45
Lbs. TiO_2/gal.	2.2	2.2	2.0	1.8	1.1	2.2
Hiding Power (sq. ft./gal)						
Wet paint (1)*	833±20	851±21	720±30	639±41	476±21	595±39
(2)**	820±24	835±22	726±28	643±67	550±41	587±42
Dry paint (1)	594±15	611±20	688±30	747±62	892±60	430±33
(2)	622±34	628±30	693±40	741±79	886±49	472±65
Oiled paint (1)	451± 9	436±12	445±11	440± 9	364±11	387±27
(2)	463±25	472±53	463±40	449±40	359±89	429±55
Kubelka Munk Scattering Coefficient ($mils^{-1}$)						
Wet	4.36±.10	4.49±.11	3.75±.10	3.27±.20	2.29±.07	3.11±.20
Dry	2.75±.06	2.83±.08	3.42±.15	3.89±.33	5.03±.30	2.11±.12
Oiled	1.62±.03	1.55±.04	1.64±.03	1.65±.06	1.33±.04	1.62±.08
Reflectivity						
Wet	87.6	87.8	87.5	86.9	85.3	87.6
Dry	84.0	84.1	86.1	87.4	89.9	85.7
Oiled	76.0	75.7	76.9	77.5	76.7	81.7
Scrub Resistance (1000 cycles)						
Coating dried 1 day	O.K.	O.K.	O.K.	O.K.	failed	O.K.
Coating aged 7 days	O.K.	O.K.	O.K.	O.K.	failed	O.K.

*Calculated by the computer from the Kubelka-Munk theory
** Calculated by the computer by regression analysis of contrast ratio versus spreading rate.

For maximum hiding power and low cost we need a high pigment volume concentration. However Lucite® Wall Paints and even "Lucite" Ceiling White are formulated at a relatively low PVC (45%). There are several reasons for this. Scrub resistance, cracking over spackle, stain removability, lap uniformity decrease with increasing pigment volume concentration.

In IO-4 type paints the decrease seems less drastic and may be acceptable in return for such advantages as better initial appearance in one coat and lower cost.

Flat Paint Composition & Properties

An attempt has been made to demonstrate the feasibility of the above ideas by the formulation of a low cost flat paint which has improved appearance* (because of better leveling and opacity) than "Lucite" Ceiling White. Appendix II shows a comparison of the composition and properties of this paint 389-H-2946 and "Lucite" Ceiling White 392-429.

Selection of Pigment Volume Concentration

The table on page 17 shows that increasing the pigment volume concentration (by the addition of extenders) increases the dry hiding power and decreases the loss of hiding power on drying. If PVC is increased too much e.g. to 75% the scrub resistance is poor and the 85° sheen is too high.

Ease of lapping and lap uniformity decrease with increasing PVC. Lapping is also worse for harder terpolymers containing external plasticizers compared to softer IO-4. However at 60-65% PVC the lapping of the externally plasticized paints seem** satisfactory compared to "Lucite" Ceiling White. Our lapping tests suggest that ethyleneglycol is definitely necessary for ease of lapping in externally plasticized flat paints at high PVC's (e. g. 65%) but perhaps unnecessary in lower PVC (e.g. 50%) paints based on IO-4.

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* Brushouts on hiding power charts and 4' x 4' Upsom boards are superior but larger scale tests with rollers on walls and ceilings are required.

** The lapping properties were determined by lapping the paints on sections of Upsom boards "primed" with a gray emulsion paint (310-125) after 4, 10 and 12 minutes. This is a very severe test for emulsion paints especially during winter months when the low humidity and the absorbency of the substrate cause rapid drying.

The higher PVC will probably result in more staining and more difficult stain removal but this disadvantage is probably not too important when balanced against the advantages of low cost, improved initial appearance and reduced cracking.

The 85° sheen results show that it is possible to eliminate the very large particle size calcium carbomate (W-90) which gives "Lucite" Wall Paints their rough texture without increasing the sheen significantly.

Selection of Thickener

The flat paint uses Thickener LN for obtaining high can consistency and good leveling at low solids (for low cost and ease of lapping). This thickener has disadvantages e. g. poor stability at elevated temperatures (140°F.), and fairly high cost. P. W. Kleinhomer (Ref. 20.) has leads however to other thickeners which should be more stable and lower in cost. A license to make these improved modifications of Thickener LN may be required from General Aniline and Film. An 11/21/67 letter (Ref. 18) was written by the writer to General Aniline and Film at the request of the Patents and Contracts Section to obtain information on their licensing plans but no reply has been received yet.

New TiO_2's for Hiding Power

Pigments Department in the last few years has had several candidates for higher hiding power.

In previous reports (Ref. 2,3) we evaluated glass-encased TiO_2, urea-formaldehyde matrix TiO_2, calcite-extended TiO_2, and the chloride process TiO_2's (Ti Pure R-900 for interior for semi-gloss paints, Ti Pure R-960 for exterior semi-gloss paints, Ti Pure R-911 for interior flat paints and Ti Pure R-902 for exterior house paints). Pigments Department now has at least 3 different approaches under investigation. These are the (1) UF matrix TiO_2, (2) Edgemoor work on new oxide treatments for chloride process TiO_2 and (3) potassium titanate milled to form a special hollow agglomerate of particles.

The last type will be evaluated in the next few weeks when a sample will become available.

The following table shows the data obtained when the 2.2 lbs. of Ti Pure R-901 in 392-429 "Lucite" Ceiling White (or Wall White) are replaced by an equal volume of the other TiO_2's.

TiO_2	Hiding Power Wet	Hiding Power Dry	Hiding Power Oiled	Scattering Coefficient Wet	Scattering Coefficient Dry	Scattering Coefficient Oiled	Code of Paint
Ti Pure R 901	595±39 615±25	430±33 460±11	378±27 -	3.11±.20 3.22±.13	2.11±.12 2.23±.02	1.62±.09 -	392-429 "
Ti Pure R-911	557± 9	448±23	351±21	2.92±.03	2.26±.09	1.73±.06	9115-52
4163-109A*	574±30	537±27	394±23	2.86±.15	2.69±.14	1.66±.10	9115-53
4163-112A*-1	599±23	494±13	394±13	3.03±.13	2.41±.09	1.62±.07	9115-54
UFT-1-AM-A**	360±12	345± 3	286± 2	1.80±.05	1.70±.03	1.18±.01	9115-75A

*New chloride process pigments with different surface treatments from Dr. A. H. Angerman (Edgemoor)

** A urea-formaldehyde matrix pigment from Dr. A. Beidins

The highest dry scattering coefficient was shown by Dr. Angerman's 4163-109A experimental grade which is a conventional chloride process TiO_2 treated with a higher concentration of hydrous oxides.

Because of the low volume concentration of TiO_2 in the U-F matrix pigment this pigment is ineffective unless it is used to replace all or most of the extenders in flat paints. Dr. R. C. Gulledge of Pigments Department (Ref. 11) recommends it be used with Ti Pure R-911 and a small amount of celite at a PVC of about 60%.

The following table shows this combination of UF TiO_2/R-911/Celite (=40/20/10 by weight) at 58% PVC was superior to a control of "Lucite" Ceiling White (45% PVC) in dry hiding power and in hiding power loss on drying.

TiO_2	Hiding Power			Scattering Coefficient			Reflectivity		
	Wet	Dry	Oiled	Wet	Dry	Oiled	Wet	Dry	Oiled
Urea-formaldehyde matrix TiO_2/ Ti Pure R-911 = 2/1 by weight	538± 8	523±19	373±16	2.65±.06	2.55±.12	1.42±.04	85.9	85.6	78.1
Ti Pure R-901 in 392-429 control	595±39	430±33	378±27	3.11±.20	2.11±.12	1.62±.08	87.6	85.7	81.7

The low values of the oiled scattering coefficient suggest that much of the hiding power of the above paints is due to pigment/ air interfaces.

The odor of formaldehyde is detectable in the UF matrix pigments. This would have to be eliminated. The cost of the matrix pigment may be too high if most of the low cost extenders have to be replaced. When samples of odor-free matrix TiO_2 are available in bigger quantities this study will be resumed.

Peeling and Cracking of Interior Wall Paints on Spackle, Calcimine etc.

"Lucite" Wall or Ceiling Paint occasionaly cracks and peels over many types of surfaces. In 1965 (Ref. 12) Sales received the following number of complaints for the following surfaces.

1965 CRACKING AND PEELING COMPLAINTS AS A FUNCTION OF SURFACE PAINTED

Surface	Number of Complaints
Old plaster (probably includes some spackle, calcimine, etc.)	488
Old Wallboard	101
New Plaster	62
New Wallboard	24
Spackle	23
Wall Paper	15

The reliability of the above data is questionable. The cost of settling these complaints is high. (Ref. 16) In 1966, 907 complaints for poor film integrity were received from the 4.5 million gallons of paint shipped.

Cracking and peeling similar to that experienced in the field can be caused by applying "Lucite" Wall Paints over a coating of calcimine. The severity of failure is increased by increasing the film thickness of the calcimine or of the "Lucite" Wall Paint. Better reproducibility has been obtained recently by applying the emulsion paints with a 20 mil clearance doctor blade over wallboard previously painted with a mixture of calcimine*/methylcellulose**/Triton X-405 (=30/5/3 by weight) in 100 parts of water.

The following data suggest that the new HG quality of "Lucite" (Wall and) Ceiling Paint 392-429 fails much less than the obsolete 392-029 quality Rhoplex AC-33/styrene-butadiene/Piccopale sold in 1965, 1966 and part of 1967 or BP quality 392-529.

	Cracking Rating*** over	
	Calcimine & methylcellulose	Calcimine/methylcellulose/Triton X-405
Present HG "Lucite" 392-429	8***	6
Obsolete "Lucite" 392-029	2	1
BP "Lucite" 392-529	2	1
HG Flowkote 389-405	9.5	9

Marketing was asked to check this predicted superiority for the present 392-429 from the current complaint data. R. L. Manley (Ref. 13) confirmed that the total complaint rate had dropped by about half since the obsolescence of the old quality, though a direct comparison of complaint data for the 2 products was not possible partly because the same labels and codes were used for the 392-029 and 392-429 qualities in 1967 when insufficient HG emulsion was available.

An attempt was made to further reduce the cracking of the HG quality by using S. Hochberg's polybutyl acrylate emulsion microgels (with and without polymethylmethacrylate) to replace the emulsions in 392-429. Unfortunately the cracking was greatly increased.

An improvement in spackle cracking resulted from the addition of certain solvents to "Lucite" Ceiling Paint or to experimental IO-4 wall paints. The following table shows xylene and some higher boiling aromatic solvents were effective.

* H. E. Milland's "Sweet Amor" brand of Calcimine from Powers and Bacher

** VM-5751

*** O-IO on scale where IO = no cracking

	Cracking Rating* over Calcimine/ Methylcellulose	Calcimine/methyl-cellulose/Triton X-405
392-429**	8*	6
" " +1% xylene	9	6
" " +2% "	10	9.5
" " +2% H-596 (hydrocarbon)	10	9.5
" " +2% H-601 (hydrocarbon)	10	9
" " +2% odorless mineral spirits	10	9
50% PVC IO-4 paint	9	7
" " " +1% H-596	10	8
" " " +2% "	10	10

* rated on 0-10 scale where 10 = no cracking or peeling.

** 392-429 = "Lucite" Ceiling Paint

Marketing and the Development Laboratory may wish to test the effectiveness of some of these solvents. The slight odor of the less volatile solvents at these concentrations may be acceptable, especially in the presence of reodorants.

High Gloss Sprayable Emulsion Paints

60° gloss in the low 80's and 20° gloss in the 50's can be obtained in IO-3 type white emulsion paints using existing mill bases, e. g. 548-961 up to about 15% PVC.

The propyleneglycol which is present in the mill base 548-961 is necessary for good coalescence and water resistance.

It can be replaced by another coalescing agent, e.g. 4% butyl carbitol H-143 which was effective in the following tests.

EFFECT OF COALESCING AGENTS ON WATER RESISTANCE OF HIGH GLOSS IO-3 PAINTS

Coalescing Agent	Gloss 60°	Gloss 20°	Scrubbed with 0.5% Ivory Flakes (Aged 1 day)	Scrubbed with 5% Bon Ami (Aged 7 days)
None	80	56	failed after 200 cycles	failed after 250 cycles
1% Butyl Carbitol (H-143)	82	57	o.k. for 1000 cycles	*
2% Butyl Carbitol	82	58	" "	failed after 750 cycles
4% " "	84	62	" "	o.k. after 1000 cycles
4% Cellosolve (H74)	*	*	failed after 300 cycles	*
4% Xylene	*	*	failed after 200 cycles	*
7% propyleneglycol	82	58	o.k. after 1000 cycles	o.k. after 1000 cycles

* Not tested

The use of propylene glycol or butyl carbitol for improving water resistance has the disadvantage of increasing the time required for the paint to become resistant to marring by masking tape. However after a 4 hour dry in the laboratory (78°F) films laid down with a 3.3 mil clearance doctor blade were hard enough not to be affected by masking tape (tape was left on for 24 hours).

A high gloss white emulsion paint was prepared for H. Grube of the Development Laboratory for evaluation as a topcoat for aircraft. This paint 9115-103P should be superior to previous emulsion candidates in water resistance, hardness (after long dries) and hiding power but because of the coalescing agents it probably cannot be taped for a few hours. The tape time will depend on the ambient drying conditions and the film thickness.

One of the difficulties with spraying emulsion paints is that they usually leave minute pin holes which become visible when the coating on glass is held up to a strong light. C. Victorius has written a backlog proposal aimed at defining this problem and if necessary solving it. Dispersing agents for pigments, emulsifying agents for the polymer may have contributed in the past to these problems. J. H. Hartshorn has shown that good dispersions of Ti Pure R-900 can be made using only traces of sodium hydroxide instead of dispersing agents. E. R. Werner, Jr. has shown itaconic acid copolymers are good dispersing agents. NaOH and itaconic acid copolymers were evaluated and found to give good dispersions of TiO_2 in water after pebble milling. Any foam disappeared after standing for a day if the viscosity was low enough. When these dispersions were mixed with IO-3 emulsion to give low PVC paints the following gloss data were obtained

Dispersing Agent for TiO_2	60° Gloss	20° Gloss	Fisheyeing
Tamol 731 (0.5 parts Tamol solids/70 parts TiO_2)	80	46	slight
Tamol 731+Amberlac 165	80	46	none
NaOH	79	49	slight
NH_4 OH	69	29	considerable
Itaconic acid terpolymer			
10 parts/70 TiO_2	40	8	"
30 parts/70 parts TiO_2	67	26	"

A disadvantage of the sodium hydroxide was that it gave dispersions which were difficult to let-down with emulsion without grit formation.

Based on the above Tamol 731/Amberlac 165 approach appears the most promising. If fisheyeing becomes a problem it may perhaps be eliminated by 3M's fluorinated surfactants FC-128 & FC-170.

A high gloss black and a high gloss blue were made without difficulty. Exhibits of these were prepared for Dr. A. Armour by spraying the coatings onto aluminum with about 50 psi air pressure. The black required a pebble milling before gloss was acceptable.

Code	Color	60° Gloss	20° Gloss
9115-43	Blue	82	60
9115-46AP	Black	78	53
9115-46A	Black	68	38

Recently the Development Laboratory has assigned H. Grube to exploit the advantages of emulsion gloss paints for Industrial Maintenance (aircraft, locomotive, gasoline stations etc.)

House Paints

By 1972 marketing (Ref. 14) would like to have a new generation of house paints "offering the present level of durability but requiring less surface preparation and fewer coats to obtain it. Ideally one coat should give good performance over chalking, cracking, blistering or peeling old paint."

In my last report (Ref. 3) formulating techniques were described for improving the leveling of IO, IO-3 or IO-4 emulsion paints.

Also the relationship between build and high shear rate viscosity was given. Photographs were shown of the better crack resistance in the accelerated weatherometer of a more flexible IO-3/Thickener LN paint (310-B-91521).

Since then an earlier modification (310-B-91453) of that paint has cracked over old paint on panels exposed 45° south in Delaware 12 months.(S-21247 exposed December 1966). The cracking is worse than for the #50 control exposed on the same panel. Similar failures have also occurred for IO, IO-3 and IO-4 paints thickened with Thickener LN. The failures are worse for the less flexible IO-4 paints. The paints based on

IO (2% MAA before imination) contain more than 5 times as much Thickener LN as the IO-4 paints, yet they crack less. It therefore appears that Thickener LN may not be as important as other factors e.g. higher acid level in causing cracking.

The cracking is between the old paint and the wood. It is worse when the old paint consists of 347-907 #39 House Paint primer/301-918 #40 House Paint than #49 Blister Resistant Primer/301-918 #40 House Paint. It is also worse for 1 coat of emulsion paint than for 2 coats of emulsion paint. When 2 coats of emulsion paint were used the failure was mostly loss of adhesion rather than cracking.

In another exposure series #21302 exposed in February 1967 instead of December 1966 failure has occurred so far only on one out of 12 panels. On each of these panels the softer IO-3 house paint 310-B-91521 and #50 are being tested side by side over cracked old oil paint.

This IO-3 paint 310-B-91521 differed from the earlier IO-3 paints which failed in S-21247 in that it contained 3% propyleneglycol which improves water resistance and scrub resistance as shown by the scrub tests on page 25. In the latest IO-3 house paint 310-H-2936 which has been exposed on 2 houses the coalescence and adhesion to chalk were improved still further by the addition of ethylene glycol monoethyl ether.

Marketing have listed (Ref. 10) the properties they would like to see improved in the next model of "Lucite" House Paint. These are better hiding, higher build, improved whiteness, better leveling, sulfide strain resistance and better mildew resistance.

These properties should be obtainable in an IO-3/Thickener LN paint with barium metaborate (Busan) replacing mica (W-88). Seed formation which occurred in a few weeks in some earlier Busan/IO-3 formulations has not occurred after 9 months on the shelf.

Effect of Triton Non-ionic Surfactants on Thickening, Stability or Adsorption

Triton X-100 (H-609) and Triton X-405 (H-766) which are made from about 10 and 40 moles respectively of ethylene-oxide are the two most commonly used nonionic surfactants in our emulsions and emulsion paints. Triton X-100 is useful for improving the freeze-thaw stability, the color development and for making paints more viscous at low solids especially when they are based on emulsions containing 3 or 4% methacrylic acid. Triton X-405 is better than Triton X-100 for decreasing the sensitivity to divalent cations e.g. Ba^{++} from barium metaborate (Busan) and for increasing the yield stress and driplessness of montmorilonite-containing wall paints. Its use in "Lucite" Wall Paint for driplessness also results in poorer leveling and worse spackle cracking.

The remarkable thickening effect of Triton X-405 even when added with considerable water to IO-3 dripless paints is illustrated by the following data.

Effect of Adding 0.5% Triton X-405 and 5% Water on Rheological Properties of a Wall Paint Containing 0.5% Triton X-100 and Veegum

Effect on Stormer Viscosity - negligible even though water added.

Effect on Viscosity at 529 $sec.^{-1}$ negligible (actually decreased from 3.6 to 3.3 poise).

Effect on Viscosity at 0.1 $sec.^{-1}$ big increase from 500 to 2200 poise.

Effect on Yield Stress - big increase from 40 to 90 dynes/sq. cm.

Although Triton X-405 even when diluted with considerable water increases the viscosity at low shear rates of Veegum-containing flat paints it has a different effect in other paints. Thus 0.6% Triton X-405 (when added to an IO-4 semi-gloss paint (389-B-91433) thickened with the usual Thickener LN) caused a decrease in viscosity from 106 to 57KU. To regain the original Stormer viscosity, 4 times the usual level of Thickener LN was required. This higher concentration of Thickener LN which was required because of the presence of Triton X-405 resulted in an increase in the brushing viscosity at high shear rates (11,000 $sec.^{-1}$) from 0.4 to 0.9 poise and no significant change in the leveling viscosity at low shear rates. Because of this increase in brushing viscosity the applied film thickness and apparent hiding power are significantly increased by this technique. The disadvantage is that the extra Thickener LN would cost about 12 cents/gallon. The ease of application might also be slightly decreased especially on porous surfaces or at low humidities.

Triton X-100 does not give much protection to IO-4, IO or HG against coagulation by multivalent cations (e.g. 5% barium hydroxide) unless more than 3% nonionic by weight on the emulsion solids are used. Triton X-405 is effective in the same test at 1% level.

Some preliminary data on the adsorption of each of these non-ionics on IO emulsion particles are shown in the following table.

ADSORPTION OF NONIONIC SURFACTANTS
ON ACRYLIC EMULSION PARTICLES

Percent of Triton added (by weight on water)	Percent Triton detected in water by ultraviolet absorption		Calculated Percent Triton Adsorbed (or absorbed) on IO Polymer	
	Triton* X-100	Triton** X-405	Triton X-100	Triton X-405
0	0.1	0.03	***	***
0.05	0.05	0	0	0.1
0.24	0.10	0.02	0.29	0.49
0.48	-	0.09	-	0.81
0.96	0.5	0.08	0.95	1.8
1.92	0.1	0.96	3.8	2.0
2.87	1.10	2.0	3.9	1.8
4.79	2.70	4.4	4.4	0.81

*Analytical Results 67-1788
** Analytical Results 67-2256
*** No Tritons were added yet the Analytical Results suggested some might be present.

The above measurements were made by Frank R. Walter using Dr. I. Hazan's modification of Rohm & Haas' suggested test method. The emulsions were sent to the Experimental Station for separation by the ultracentrifuge into a supernatant clear layer which was analysed by UV absorption spectroscopy. These results suggest that more Triton X-100 than Triton X-405 (on a weight basis and especially on a mole basis) is absorbed or adsorbed at the higher concentrations. However more Triton X-405 may be adsorbed at lower concentrations of these surfactants. These tentative observations are being checked by a duplicate set of analyses. The literature on adsorption of similar polyoxethylated octylphenols (Ref. 17) suggests that adsorption (on quartz) decreases as the solubility in water is increased by increasing the proportion of ethylene oxide.

A better understanding of the role of non-ionic surfactants in emulsion paints is desirable. They have an important effect on stability, color development, efficiency of thickeners and their continued use in IO and HG paints will necessitate a royalty payment of about $100,000/year. A proposal (Ref. 15) has been written for further study of this royalty question.

GLOSSARY

Hiding Power, - Number of square feet over which a gallon of paint can be uniformly spread to produce the specified contrast ratio, C = 0.98.

Contrast Ratio, C, - Ratio of the reflectance of a paint film over black substrate of 5 per cent or less reflectance, to the reflectance of the same paint, equivalently applied and dried, over a substrate of 80 per cent reflectance.

Reflectivity, R_{oo}. - The reflectance of a film so thick that a further increase in thickness does not change the reflectance.

The Kubelka-Munk theory relates the reflectance, R, of a paint film at any thickness, by means of two coefficients: a scattering coefficient S, and an absorption coefficient, K. The absorption coefficient is defined as the limiting value of the rate of decrease of transmittance per unit colorant layer thickness as the thickness approaches zero.

$$K = (dT_i/dX)_{X \to 0}$$

The scattering coefficient is defined as the limiting value of the rate of increase of reflectance per unit thickness as the thickness approaches zero, the layer being backed by an ideal black backing.

$$S = (dR_o/dX)_{X \to 0}$$

The scattering is due primarily to the pigment in the paint whereas the absorption is due to both the pigment and the vehicle. When a paint film is so thick that a further increase in thickness does not change its reflectance, then this reflectance is known as its reflectivity, R_{oo}. For such a thick film, S, K, and R_{oo} are related by

$$K/S = (1-R_{oo})^2/2R_{oo}$$

PVC - Abbreviation for Pigment Volume Concentration which is the % pigment expressed on the total volume of paint solids.

MMA - Methylmethacrylate

2EHA - 2-ethylhexylacrylate

MAA - Methacrylic acid

PI - Propyleneimine

GLOSSARY (CONT'D)

IO - MMA/2EHA/MAA = 45/53/2 (PI/MAA = 2/1) RC-11005

IO-3 - MMA/2EHA/MAA = 47.5/49.5/3 (PI/MAA=3/1) (RC-11013 or RC-11014)

Softer IO-3 - MMA/2EHA/MAA = 45/52/3 (" " ") (RC-B-87437)

HG Emulsion MMA/2EHA/MAA = 44/54/2

Piccopale hydrocarbon emulsion - G-1117

Thickener LN (reaction product of a nonionic surfactant alcohol and methyl vinyl ether/maleic anhydride) _ G-1144

APPENDIX I

Effect of Ridges and Valleys of Brushmarks on Apparent Hiding Power

Emulsions paints especially the dripless varieties have poor leveling and this makes the apparent hiding power when brushed or rolled worse than the hiding power measured in the laboratory. Laboratory hiding power measurements are made on films laid down uniformly with wire-wound rods. The reflectances are measured on an instrument (colormaster) which is not as sensitive as the eye to the valleys caused by brushing. The leveling was so poor in "Lucite" Ceiling White (392-029 quality) that the average film thickness in the valleys* was only 60% (± 5%) of the thickness in the ridges. The effect of this on hiding power and contrast ratio is shown below.

	Valleys	Ridges
Film Thickness	1.03±0.25 mils 560 sq. ft./gal.	1.73±0.34 mils 334 sq. ft./gal.
Spreading rate Calculated Contrast Ratio when wet	0.99	0.99
Apparent Hiding Power while wet	Excellent	Excellent
Calculated Contrast Ratio when dry	0.97	0.99
Apparent Hiding Power when dry	fair	excellent

*Measured with the slit microscope for a film brushed on glass.

APPENDIX II

COMPARISON OF THE PROPERTIES OF A LOWER COST FLAT EXTERNALLY PLASTICIZED ACRYLIC EMULSION PAINT WITH "LUCITE" CEILING WHITE

Code	Experimental 389-H-2946	"Lucite" Ceiling White 392-429
Binder		
MMA/2EHA/MAA	60/36/4 (iminated)	44/54/2 (uniminated HG)
Others	benzyl butyl phthalate	Piccopale
Pigment Volume Conc.	65%	45%
TiO_2/gal.	1.81bs. Ti Pure R-911	2.2 lbs. Ti Pure R-901
Extenders	W10 11/W1002	W1012/W90/W1011/W1o14/ W-192
Thickeners	Thickener LN	methylcellulose + montmorilonite + Acrysol
Solids (by volume)	31.9%	33.9%
" (by weight)	51.4%	50.3%
Gallon Weight	11.58	11.08
Raw material Cost of Ingredients*	$1.24 (Approx.)	$1.41 (Approx.)
Bulk mill cost	$1.41 "	$1.58 "
Stormer Viscosity	108 Krebs Units	85 Krebs Units
Viscosity (0.1 sec^{-1})	900 poise	1600 poise
" (13000 sec^{-1})	0.7 poise	0.6 poise
Yield Stress	0	70 dynes/cm^2
Ease of lapping	good	very good
Lap uniformity	good	very good
Leveling	very good (brushed) good (rolled)	fair (brushed) poor (rolled)
Driplessness	drips but only slowly because of high consistency	very good
Tendency to splatter when rolled too fast	bad	very bad
Texture	fairly smooth	rough
85° Sheen	2.6	1.3

*Includes manufacturing cost of base (pigment dispersion).

Hiding Power		
Wet	646±32	595±39
Dry	552±21	430±33
Oiled	356±12	387±27
Appearance on Hiding Power Chart		
(a) When brushed	very good uniformity	poorer apparent hiding power
(b) When rolled	fair uniformity	poor uniformity
Resistance to cracking over calcimine	very good	good
Scrub Resistance		
Aged 1 day	passed 1000 cycles	passed 1000 cycles
" 7 days	" " "	" " "
Resistance to staining	poorer	fair
Ease of stain removal	poorer	fair

APPENDIX III

LOW COST, EXTERNALLY PLASTICIZED, FLAT ACRYLIC EMULSION PAINT 389-H-2946

	lbs./100 gal.
Pigment Dispersion 9115-183	799.60
Tap water	35.40
Triton X-100	1.70
Ethyleneglycol	32.40
Thickener LN	22.20
Benzyl butyl phthalate	18.10
Emulsion RC-B-91484	158.90
Hydrocarbon solvent H-596	22.20
Defoamer G-817	0.90
28% Ammonia	2.70
Tap Water	63.90
	1158.00

PVC = 65%

Solids (by volume) 31.9%

Solids (by weight) 51.4%

TiO_2/gal. 1.8 lbs.

APPENDIX III (CONT'D)

"48 PROCESS" PIGMENT DISPERSION 548-H-2944 FOR LOW COST FLAT ACRYLIC EMULSION PAINT

Tap water	35.54
Odorless mineral spirits	1.17
Triton X-100	.33
Tamol 731	.94
Phenyl mercury proprionate	.01
Ti Pure R-901	22.35
28% Ammonia	.29
Celite Silica W-1011	17.35
Defoamer G-817	.26
Black colorant W-247	.01
Aluminum silicate W-1002	21.75
	100.00

PVC	96.73%
Solids (by volume)	36.93%
Solids (by weight)	62.29%

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20. P. W. Kleinhomer R-68-5

21. E. R. Werner, Jr. R-68-2

FIGURE 1

392-429 (P-760040) "LUCITE®" CEILING WHITE

EFFECT OF SHEAR RATE ON APPARENT VISCOSITY

(from 3.3 sec.$^{-1}$ to 529 sec.$^{-1}$ & from 529 sec.$^{-1}$ to 3.3 sec.$^{-1}$)

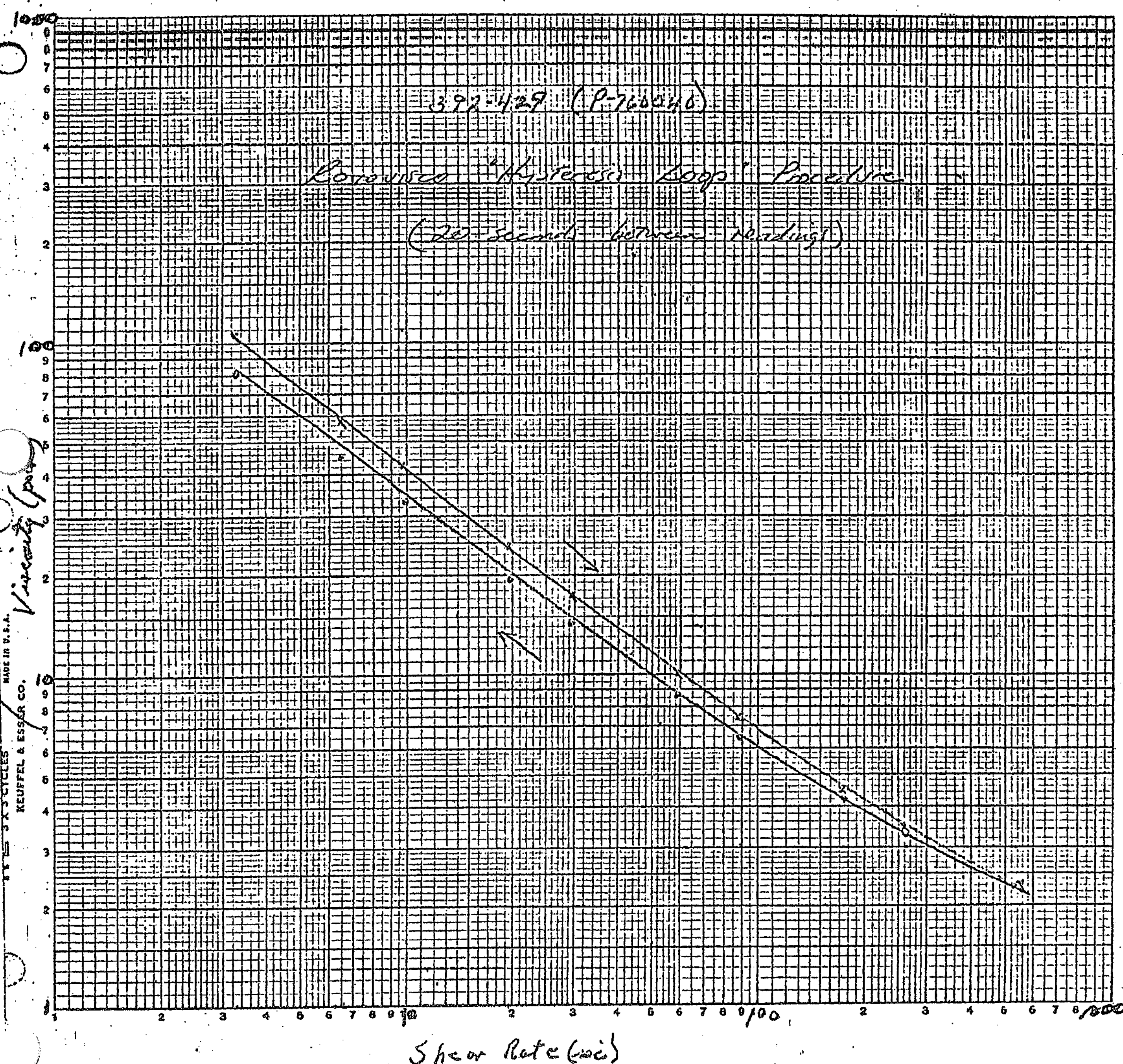
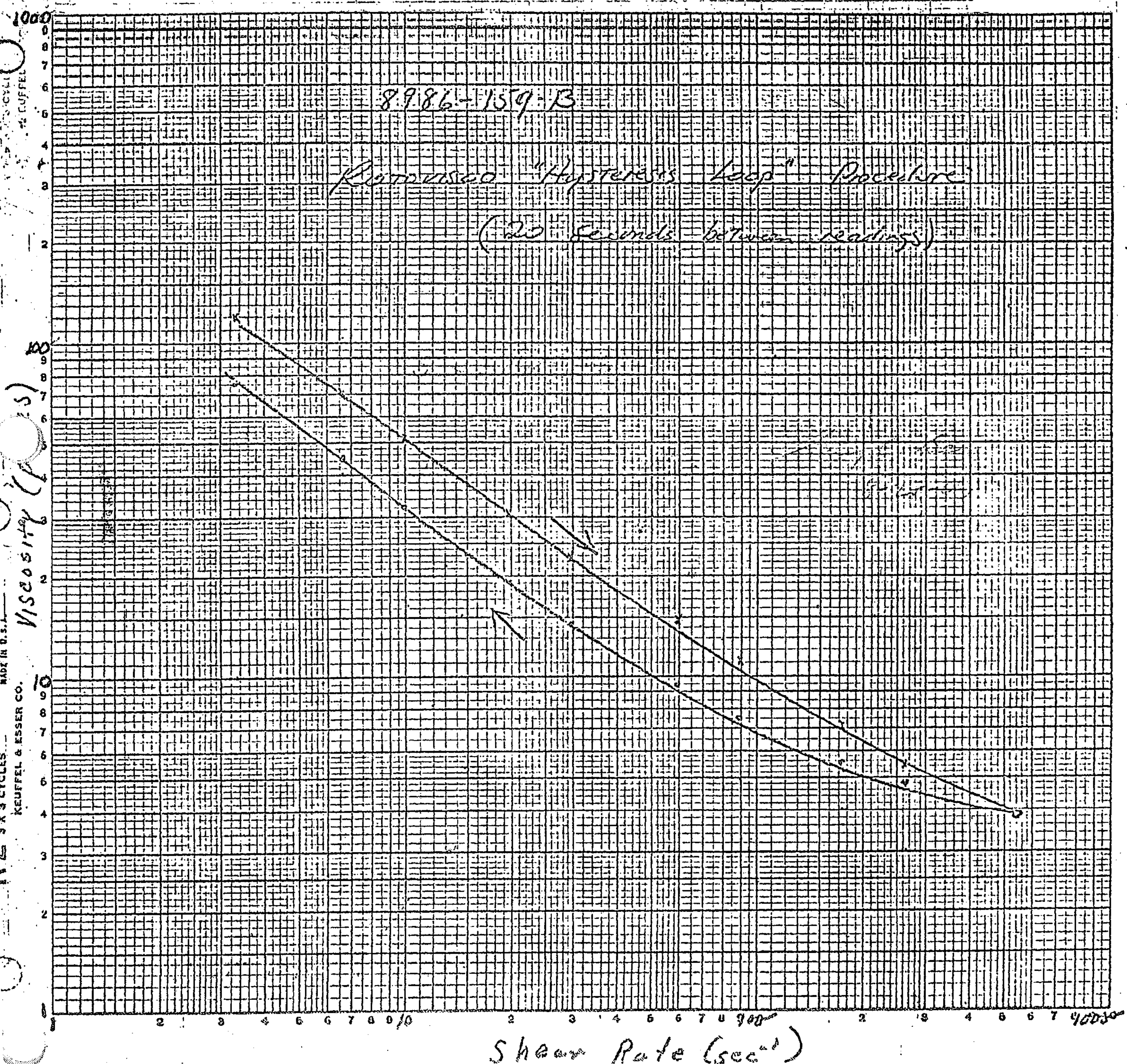


FIGURE 2

8986-159B (MODIFIED IO-3/VEEGUM PAINT)

EFFECT OF SHEAR RATE ON APPARENT VISCOSITY

(from 3.3 sec.$^{-1}$ to 529 sec.$^{-1}$ & from 529 sec.$^{-1}$ to 3.3 sec.$^{-1}$)



Guy C. Bell, Jr.

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