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FINAL REPORT

DEVELOPMENT OF A LIQUID POLYVINYL ACETATE PAINT

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THE REARDON COMPANY
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FOREWORD

On January 1, 1954, Mr. Fred L. Keck under the supervision of Dr. L. L. Carrick began an investigation of moisture control paint. The initial work was directed toward the development of a dry polyvinyl acetate base paint that once dispersed in water and applied could not be re-emulsified. Work continued along these lines until March 3, 1954, at which time Mr. C. Clark of the Reardon Company's Product Development Department advised during his visit to our laboratories that development of a liquid polyvinyl acetate masonry paint (similar to Gelvatex) should take precedence over a dry powder paint. This statement, that our work should be on the development of a liquid polyvinyl acetate masonry paint, was reaffirmed by Mr. Ben Zmuda, Reardon's research director, during his visit on April 15, 1954.

Messrs. H. Davis, B. Zmuda, and C. Clark of the Reardon Company visited our laboratories on August 23, 1954, and advised that the Reardon Company had decided against marketing a liquid polyvinyl acetate paint. As a result, that phase of the project (i.e., development of a liquid polyvinyl acetate paint) was closed. On the ensuing pages may be found a summary of the work done on the development of a liquid polyvinyl acetate paint.

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DEVELOPMENT OF A LIQUID POLYVINYL ACETATE PAINT

Preliminary investigation of the Gelvatex polyvinyl acetate paint samples submitted by the Reardon Company revealed the following information.

pH: Range from 6.2 for white to 6.5 for bisque. (White after 7 months storage had a pH of 6.5; however it had developed an acetic odor and a lumpy consistency. Long term stability is questionable.)

Total solids: Range from 40.3% for cactus green to 44.3% for white.

Water content: White sample only, 55.7%.

Pigment analysis: White sample only. Free silica (no silicates); approximately 63% (TiO_2).

PVA content: No successful method for extracting (isolating) the polyvinyl acetate was found.

Evaluation of Water Resistance of Polyvinyl Acetate Latices

An initial examination of the water resistance of various polyvinyl acetate latex films (without any film conditioning agent such as plasticizer and/or solvent) was made. Of the commercial polyvinyl acetate latices investigated, Colton's Vinac WR-20 gave the best water resistance by itself. However, this material also displayed a tendency to skin in the container. The next best latices as far as water resistance was concerned were Bakelite's WC-130 and Dewey and Almy's Everflex G. The water resistance of all latices except those containing polyvinyl alcohol, a protective colloid, improved on addition of a film conditioning agent such as dibutyl phthalate.

Investigation of Dispersion Methods

Examination of the mixing procedures and basic polyvinyl acetate formulations suggested by the various latex manufacturers was conducted. These formulations with slight modifications are found on pages 13 through 20 of the appendix. Included with the formulations are the mixing procedures, observations, approximate costs as of June 1, 1954, and other pertinent data.

In formulating the polyvinyl acetate paints, three methods were used for pigment dispersion: colloid mill, ball mill, and 3-roll mill. In general, entrapped air was a major difficulty especially where no antifoam agent was used. The degree of air entrapment was very bad in the colloid mill and ball mill and required weeks to work its way out of the paint. Depending on the formulation, dispersion by the 3-roll mill produced pigment dispersion containing negligible to objectionable quantities of entrapped air.

In the Bakelite formulation where the dispersing agent was of the sulfonate type, it was found that entrapped air could be eliminated by adding the protective colloid (thickening agent) after the pigment had been dispersed. Probably a small portion of protective colloid could be present during pigment dispersion without causing entrapped air, but no study was made of the critical amount. Entrapped air also resulted when a nonionic dispersing agent such as Tergitol NP-35 was used as a pigment dispersing agent. In some cases the presence of a defoamer before dispersion prevented excessive entrapped air. An acrylic paint using Rohm and Haas' polymer Rhoplex AC-33 is very susceptible to foaming. Essentially an air free dispersion containing an antifoam agent can be made on a 3-roll mill, but other means of dispersion create excessive entrapped air.

A series of paints employing varying procedures were made up according to the following basic formula.

Ingredient	Percent	Lbs/gal	Cost/lb	Gallons	RMC/100 lbs
Water	20.1	8.33	---	2.416	---
Daxad 11	0.2	---	.25	---	.05
TiPure R-510	20.0	34.99	.245	0.572	4.90
ASP 400	7.5	21.66	.02	0.347	.15
Metronite BXXXX	8.0	23.74	.0175	0.337	.14
Ethylene glycol	2.9	9.3	.1875	0.312	.54
*WC-5510	27.6	9.10	see below	3.035	6.14
Cellosize WPHS 5%	13.0	8.33	.48	1.560	.31
Glyoxal 30%	0.6	10.48	.185	0.057	.11
Tergitol NPX	0.1	8.8	.315	0.011	.03
	100.0			8.647	12.37

*Composition of WC-5510:

	Lbs	Lbs/gal	Cost/lb	Gallons	RMC
WC-130 latex solids	14.4	9.94	.39	1.46	5.62
Dibutyl phthalate	1.44	8.75	.3575	0.165	.52
Water	11.76	8.33	---	1.41	---
	27.6			3.035	6.14

Pigment = 35.5%
Vehicle = 64.5%
Vehicle nonvolatile = 26.3%
PV = approximately 43.6%
Lbs/gal = 11.55
Viscosity = 76-82 KU
Ratio of pigment to nonvolatile vehicle solids:
By volume 1 : 1.3
By weight 1 : 0.45
2.31 lbs TiO_2/gal
1.66 lbs WC-130 solids/gal
5.12 lbs water/gal
Cost = approximately $1.43/gal

The order of dispersion found to be most satisfactory is as follows.

1. Dissolve the dispersing agent in the water.

2. Add pigments and fillers to No. 1 with stirring to insure wetting.

3. Disperse these materials by any suitable means. In the case of 3-roll mill dispersion some water should be withheld to insure a satisfactory pigment paste.

4. The remaining components, ethylene glycol, plasticized latex WC-5510, Cellosize WPHS, Glyoxal, Tergitol NPX, and any previously withheld water, should be added in sequence making sure that each is thoroughly dispersed before the next addition.

Dispersion on a 3-roll mill caused no entrapped air even when Cellosize WPHS was present in the pigment dispersion. The same is true when plasticized latex WC-5510 was also included. However, the inclusion of the latex in the pigment dispersion resulted in a completed paint having a viscosity of 72 KU compared to 76 KU for a paint having the plasticized latex WC-5510 added after pigment dispersion. The paint regardless of preparation shows a slight tendency to thixotropy.

In the colloid mill and ball mill, foaming resulted when Cellosize WPHS and/or plasticized latex WC-5510 were present. Addition of these items after dispersion eliminated entrapped air. Hence, the pigment dispersion should contain water, dispersing agent, and pigments only. Following this rule the viscosity of a paint whose pigment was dispersed in a ball mill was 82 KU. Using the colloid or 3-roll mill, the viscosity was usually 76 KU. This viscosity difference is probably the result of the fineness of grind.

	Fineness (Hegman Scale)
Colloid or 3-roll mill	4.5
Ball mill	6.5

It is interesting to note that after four months aging, the two paints (KU of 76 and 82) did not alter viscosity and were easily redispersed into a very smooth flowing paint. When the plasticized latex WC-5510 was substituted with 10% dibutyl phthalate plasticized Shawinigan Latex TS-22, the paint showed greater settling. Difference in latex viscosity and the extent of compatibility with the paint formulation probably attributed to the greater settling.

The formulation on pages 2 and 3 was modified by adding three parts of zinc oxide (Kadox 15) and decreasing the TiO_2 the same amount by weight. The finished paint was very thixotropic, but fluid on stirring with an initial viscosity of 83 KU. After four months storage the paint is still stable and shows no increase in viscosity. Difficulty encountered in dispersing the zinc oxide was overcome by adding ethylene glycol to the pigment prior to milling.

A series of paints substituting various quantities of Cellosize WP-300 for Cellosize WPHS and corresponding quantities of water were made. Included in the series was a direct substitution of a 3% solution of Cellosize WP-300 for the 5% solution of Cellosize WPHS. This substitution seemed logical, since both solutions have the same viscosity as measured on a modified Krebs Stormer Viscosimeter. However, in all instances, standing for ten days or so produced a thickened paint that could not be satisfactorily redispersed. It was decided at this time that some fundamental data would have to be determined since the trial-and-error method of formulating leaves much to be desired. Literature references were of no assistance in supplying necessary data.

Pigment Water Demand

The water demand, arbitrarily taken as the amount of water containing a given percentage of dispersing agent necessary to make a fluid paste which will fall from the end of a spatula, of various pigments and fillers with various wetting agents was determined. At the same time the nature of the pigment paste such as consistency, ability to flow, dilatancy, foaming tendency, etc., were noted. In addition, surface tension data of various dispersing and wetting agents at different concentrations and in combination with antifoam agents were determined. Data on water demand and surface tension may be found in the appendix beginning on page 21.

Preliminary investigation on water demand of the titanium dioxides disclosed that TiPure R-510 and Unitane OR-540 required the least amount of water for dispersion. Knowledge of the water demand of the various pigments provides for an estimate of the free available water present in any polyvinyl-acetate system. The viscosity of the system is dependent on this free available water. Preliminary investigation of surface tension indicated that these data can be useful in predicting water demand. It was found that the lower the surface tension the greater the pigment water demand. Two zinc oxides, New Jersey Zinc's Kadox 15 and XX505, did not show dilatancy regardless of the dispersing agent used and hence are promising pigments. From the preliminary data it appears that dispersing agents having high surface tensions produce dilatant dispersions with some zinc oxide pigments. All dilatant zinc oxide dispersions impart dilatancy when added to plasticized latex WC-5510. Further addition of a thickening agent such as Cellosize WPHS resulted in rapid viscosity increase. The resultant paste which resembles "silly putty" is of questionable value in polyvinyl acetate paints. A small quantity of nondilatant zinc oxide dispersion added to titanium dioxide produces a satisfactory pigment paste. Because zinc oxides are reactive pigments, large quantities and dilatent types may promote unstable systems.

Of the fillers, Metronite BXXXX, magnesium calcium carbonates, and silicates had the lowest water demand and showed excellent flow. ASP 400 appears to be the most promising of the clays examined. Lorite, calcium carbonate plus diatomaceous silica, might be considered, although Metronite BXXXX and ASP 400 appear to be by far the best fillers. As dispersing agents, Daxad 11, Blancol, and similar condensed naphthalene sulfonates appear very satisfactory. Nonionics, alkyl aryl polyethylene glycol ethers, are not as efficient and have a tendency to produce a foamy dispersion. For dispersion of some organic pigments, nonionics may be necessary to obtain the best color.

Adhesive and Cohesive Force Phenomenon

Early investigation of the Gelvatex samples revealed that there was a powerful attractive force exerted between the pigment and the polyvinyl acetate latex. As a result, no solvent tried (including Carbitol) would extract all the polyvinyl acetate from the pigment. Paints having the basic formulation listed on pages 2 and 3 behaved the same way. In each case sufficient polyvinyl acetate remained to impart strength and toughness to the pigment mass. It was thought that there was a critical amount of polyvinyl acetate, as a monomolecular layer, absorbed on any given surface area of pigment and an attempt was made to determine whether there was a critical amount and, if so, the quantity.

In attempting to duplicate the adhesive force phenomenon it was found that addition of the extracting medium, Carbitol, to the paint caused heat generation in most cases. An addition to the pigment polyvinyl acetate slurry (water, pigment and polyvinyl acetate) of dispersing agent, such as a protective colloid, vinyl acetate monomer, extender pigments, diphenylamine (vinyl acetate monomer inhibitor), ammonium polyacrylate, alcohol, and various combinations of these materials, did not produce strength and toughness in the extraction treated pigments. The polyvinyl acetate latex was for all practical purposes completely extracted from the pigment mass leaving no strength. It was noted, however, that the addition of vinyl acetate monomer followed by the polyvinyl acetate latex did impart more strength to the pigment mass than any other combination. Also of interest is the fact that the addition of ammonium polyacrylate allowed the pigment mass to be easily crumbled and this fact may be helpful in developing a dry polyvinyl acetate paint. Another interesting fact was that Carbitol added to a pigment slurry containing water did not extract the polyvinyl acetate latex. Evidentally a water-Carbitol mixture is not as good for extraction purposes as a straight Carbitol.

Aging of Vehicle Systems

Since Bakelite suggests the addition of ammonium polyacrylate to a paint, aging studies on different vehicle combinations were initiated. It was found that the viscosity and surface tension of the vehicle (all materials in a finished paint except pigments and fillers) did not change on aging for 100 hours at 120°F. However, a vehicle similar to the one appearing on pages 2 and 3 separated into two layers, while a similar formulation containing ammonium polyacrylate did not result in settling or layering. Consequently the function of the ammonium polyacrylate is one of suspension stability and not necessarily as a thickening agent.

More Important Formulations

The following formulation was made up just prior to discontinuing the development of the liquid polyvinyl acetate phase of the project.

TiPure R-510	19.5
ASP 400	9.8
Tergitol NP-35	0.3
Water	31.1
Ethylene glycol	2.36
WC-5510	28.3
K-707 (15% T.S.)	2.64
Carbitol	1.7
Cellosize WP-300 (5%)	4.3
Daxad 11	Trace
	100.0

Mixing Procedure:

1. To the pigment add Tergitol NP-35, Daxad 11 and sufficient water for ball milling (about 75%). Grind overnight and discharge into mixing tank.

2. With adequate agitation add the remaining constituents in the following order: ethylene glycol, plasticized latex WC-5510, K-707 (ammonium polyacrylate), Carbitol, Cellosize WP-300, and the remaining water.

A paint processed according to the above formulation (similar to Bakelite's suggestion) exhibited excessive foaming because Tergitol NP-35, a nonionic, was present during the pigment dispersion. It took three weeks for the foam to work its way out of the paint at which time the paint looked very good. Initial viscosity and the viscosity after aging for one month were essentially the same, 75 KU.

Because of the foaming tendency the paint was reformulated using an increased amount of Daxad 11, eliminating Tergitol NP-35, and decreasing the water content to give an initial viscosity of 75 KU. The paint exhibited no foam and looked very promising. However, on aging for a month the viscosity increased to 107 KU which means that more water must be present initially to maintain viscosity stability.

A formulation similar to the formula on pages 2 and 3, except Cellosize WPHS is replaced by Cellosize WP-300, appeared very satisfactory after storing for one month. The viscosity had not changed, being about 67 KU. Because this pigmentation is very promising and because of the fact that ammonium polyacrylate appears beneficial, a paint using the following formulation and procedure was made.

TiPure R-510	20.0
ASP 400	7.5
Metronite BXXXX	8.0
Water	20.1
Daxad 11	0.2
Ethylene glycol	2.5
WC-5510	28.3
K-707 (15% T.S.)	2.6
Carbitol	1.7
Cellosize WP-300 (5%)	4.0
Tergitol NPX	0.1
Water	5.0
	100.0

Mixing Procedure:

1. Items through Daxad 11 were ball milled overnight.

2. Discharge into a mixing tank and add the remaining items in the order listed with constant agitation.

The addition of the plasticized latex WC-5510 causes the pigment slurry to become very viscous. The K-707 increases the viscosity still more, but continued stirring results in a fluid slurry. It is imperative to have adequate stirring; otherwise lumps will remain and these will persist in the finished paint. This paint has a pigment volume of 42.6 which is probably too near the outer range to be satisfactory. No long range storage data are available other than that the initial viscosity of 70 KU has not changed in three weeks.

EXPERIMENTAL RESULTS

Polyvinyl acetate paint films are noted for their permeability, that is, ability to transmit water vapor. For comparison purposes the "specific permeability", defined as the number of milligrams of water which have permeated through one square centimeter of film of one millimeter thickness in 24 hours, was determined on the following polyvinyl acetate systems.

TABLE I

POLYVINYL ACETATE FILM PERMEABILITY

Sample	Specific Permeability	Conditions of Test Film
National Starch (submitted by Reardon)	207	1
Gelvatex ash	156	1
Gelvatex cactus green	128	1
Gelvatex bisque	159	1
Gelvatex white	140	1
Gelvatex white	111	2
Shawinigan 201	137	2
WC-5510	145	2
TS-22 plus 10% dibutyl phthalate	92	2
Formula pages 2 and 3 with WC-130	195	2
Formula pages 2 and 3 with TS-22	197	2

1. Films were cast on a tin panel, removed by stripping in a mercury bath, aged two days at room temperature (around 70°F), and then placed in a Payne permeability cup. Test was run at room temperature (average 70°F).

2. Films were cast on a tin panel, aged 90 hours at 120°F, removed by stripping in a mercury bath, and then placed in a Payne permeability cup. Test was run at room temperature (average 78°F).

It is interesting to note from the above data that aging of the white Gelvatex sample resulted in lower vapor transmission. This was probably the result of part of the plasticizer being lost from the film. Polyvinyl acetate paints having high pigment volumes (formulation on pages 2 and 3) have higher permeabilities. Plasticized latex WC-5510 and similarly plasticized Shawinigan latex TS-22 should have approximately the same specific permeability. These latices are supposedly very similar in nature.

Several polyvinyl acetate paints were applied in one and two coat systems on asbestos shingles and exposed on the roof of the East Engineering Building, University of Michigan. The asbestos shingles which had been weathered for five years were prewet before the polyvinyl acetate paints were applied in order to eliminate pinholing. The panels were held in the test rack at an angle of 45° facing towards the south. To date there is no difference in exposure results between the one and two coat systems. Data representative of both systems are found in Table II.

TABLE II

EXTERNAL EXPOSURE RESULTS

Formulation	Months Exposed	Checking	Chalking	Hiding* Power
1. Dupont, pages 14 and 15	3	None	Yes	8
2. Gelvatex white	3	None	None	7
3. Shawinigan 201	3	None	None	7
4. Rohm and Haas, pages 17 and 18	3	None	Yes	8+
5. Bakelite, pages 19 and 20	3	None	None	7
6. Basic formula, pages 2 and 3				
a. With WC-5510	3	None	None	8
b. With TS-22	3	None	None	8
c. With zinc oxide substitution	3	None	None	9
d. With Cellosize WP-300	1	None	None	8
7. Basic formula, page 7 with Daxad 11	1	None	None	8
8. Basic formula, page 8	1	None	None	9

*10 = best; 0 = complete failure

The paint rack itself made of white pine and hemlock was painted with the following systems.

Primer	Topcoat
1. White lead	White lead
2. White lead	Polyvinyl acetate (formula, pages 2 and 3)
3. Polyvinyl acetate	White lead
4. Polyvinyl acetate	Polyvinyl acetate (formula, pages 2 and 3)
5. Polyvinyl acetate	Acrylic (Rohm and Haas formula, page 17)

It is interesting to note that checking occurred in system No. 4: polyvinyl acetate primer-polyvinyl acetate topcoat. These checks were grain checks. No checks were visible after 3-1/2 months in the other systems. The two systems having a polyvinyl acetate topcoat were cleaner than the others.

Films of polyvinyl acetate paints applied on white pine panels and exposed in an Atlas Weatherometer also showed grain checks. This occurred when the panels were not backed and also when entirely coated with polyvinyl acetate paint.

CONCLUSIONS

Long term exposure data are not available but rather data on limited exposure; the results of which are not significant.

It appears that the addition of ammonium polyacrylate to the paint is beneficial in that it helps prevent settling and at the same time improves the hiding power.

The last formulation developed which is found on page 8 offers the most promise, however the exposure was for only 30 days. It incorporates the best materials tested so far: ammonium polyacrylate, ASP 400, Metronite BXXXX, Daxad 11, and Cellosize WP-300. The application qualities of this paint were very satisfactory.

A variation of the formulation on pages 2 and 3, that is, the substitution of three parts zinc oxide for titanium dioxide on a weight basis, is also very promising, especially if increased resistance to ultra-violet light is desired.

Since there was no breakdown of film integrity during the first 3 months of external exposure, the exposure of the polyvinyl acetate panels on the roof of the East Engineering Building should be continued.

APPENDIX

MODIFIED NATIONAL STARCH FORMULA 4C

Ingredient	Percent	Lbs/gal	Cost/lb	Gallons	RMC/100 lbs
TiPure R-510	23.9	34.99	.245	0.683	5.85
Asbestine 3X	6.9	23.74	0.0175	0.291	.12
Mica 325 w.g.	1.0	23.49	0.0775	0.040	.08
Monoammonium phosphate	0.6	15.0	1.01	0.040	.61
Tergitol NPX	0.1	8.8	.315	0.011	.03
Resyn 12K51	32.7	9.1	.22*	3.595	7.19
Diethylene glycol	1.0	9.31	.2025	0.107	.20
Cellosolve	2.0	7.74	.20	0.259	.40
Glyoxal 30%	0.5	10.48	.185	0.048	.09
Water	27.3	8.33	---	3.280	---
Acrysol GS	4.0	8.9	.125	0.450	.50
	100.0			8.804	15.07

*Estimated cost of Resyn 12K51.

Pigment = 31.8%
Vehicle = 68.2%
Vehicle nonvolatile = 29.1%
PV = approximately 35.7%
Lbs/gal = 11.36
Viscosity = 93 KU
Ratio of pigment to nonvolatile vehicle solids:
By volume 1 : 1.8
By weight 1 : 0.567
2.72 lbs TiO_2/gal
2.05 lbs Resyn 12K51 solids/gal
5.21 lbs water/gal
Cost = approximately $1.71/gal

Mixing Procedure

1. Dissolve monoammonium phosphate in a portion of the water.
2. Add pigments and fillers to (1) with constant agitation.
3. Add remaining water with constant agitation.
4. Add diethylene glycol, Cellosolve and Acrysol GS with constant agitation.
5. Add Tergitol NPX with constant agitation. Complete the dispersion by passing through a 3-roll mill.

6. Add Resyn 12K51 with constant agitation.

7. Add glyoxal with constant agitation.

Observations

Initial viscosity was 93 KU. Lowering the Acrysol GS content did not appreciably lower the viscosity. Initially all viscosity variations produced by the addition of Acrysol GS resulted in smooth paints that were thixotropic. On aging a week they develop soft agglomerates. Shortly thereafter the paints approached a consistency of custard, making them useless. The exact cause was not established, but it may have been the Resyn 12K51 itself. Acrysol GS, a sodium polyacrylate, will coagulate when in contact with small quantities of a weak acid such as acetic. The sample of Resyn 12K51 on aging did develop an acetic odor and became very viscous indicating an unstable system. The most common cause of unstability was a poor emulsion stabilizer. Replacement of Acrysol GS with carboxymethyl cellulose or another thickening agent would probably result in a more satisfactory paint, but no further work was done with Resyn 12K51 since other latices appeared better. Also a sample of a paint known as formula 3A submitted by National Starch was not satisfactory.

Pigment dispersion made in a colloid mill instead of a 3-roll mill resulted in entrapped air.

MODIFIED DUPONT FORMULA

Ingredient	Percent	Lbs/gal	Cost/lb	Gallons	RMC
(TiPure FF	4.8	32.32	.225	0.149	1.08
(TiPure R-610	19.0	34.99	.245	0.543	4.65
(Mica 325 mesh w.g.	2.7	23.49	0.0775	0.115	.21
(Methocel 400 (5%)	11.1	8.34	.66	1.330	.37
(Balab 259	0.2	8.50**	.40**	0.024	.08
(Water	14.3	8.33	---	1.716	---
Emulphor EL-719	0.2	8.85**	.36	0.023	.07
Water	7.1	8.33	---	0.852	---
(Aerosol OT (100%)	0.2	9.0**	1.00	0.022	.20
(Carbitol	3.2	8.55	.2075	0.375	.66
(Water	0.8	8.33	---	0.096	---
Elvacet 81-900	32.9	9.2	0.215**	3.580	7.07
Dibutyl Phthalate	2.7	8.75	.3575	0.309	.97
	99.2*			9.134	15.36

*"Dowicide" A preservative was not included. Paint made with "Dowicide" B preservative caused agglomeration.

**Figures estimated.

Pigment = 26.5%
Vehicle = 73.3%
Vehicle nonvolatiles = 30%
PV = approximately 27.7%
Lbs/gal = approximately 10.85
Viscosity = 82 KU
Ratio of pigment to nonvolatile
vehicle solids:
By volume 1 : 2.62
By weight 1 : 0.786
2.61 lbs TiO_2/gal
1.99 lbs Elvacet 81-900 solids/gal
5.20 lbs water/gal
Cost = approximately $1.68/gal

Mixing Procedure

1. Add with constant agitation the pigments and fillers to the Methocel followed by water and then Balab 259.

2. Disperse on 3-roll mill.

3. Dissolve Emulphor EL-719 in water and add to pigment dispersion with constant agitation.

4. Aerosol OT dissolved in Carbitol and water and added to pigment dispersion with constant agitation.

5. Dibutyl phthalate plasticized Elvacet 81-900 added with constant agitation.

Observations

Foaming occurred when the pigment was dispersed in a colloid mill in the presence of Emulphor EL-719. No foaming occurred in the above mixing procedure. Paint is thixotropic and has an initial viscosity of 82 KU. After four months storage the paint was easily redispersed. However, its viscosity had increased to 100 KU which is too high for satisfactory application.

MODIFIED COLTON CHEMICAL FORMULA

Ingredient	Percent	Lbs/gal	Cost/lb	Gallons	RMC
Vinac WR-20	32.9	9.2	0.215**	3.580	7.07
Dibutyl Phthalate	2.7	8.75	0.3575	0.309	.97
TiPure R-610	23.8	34.99	0.245	0.680	5.83
Mica 325 mesh w.g.	2.7	23.49	0.0775	0.115	.21
Methocel 400 (5%)	11.1	8.34	.66	1.330	.37
Water	14.3	8.33	---	1.716	---
Emulphor EL-719	0.2	8.85**	.36	0.023	.07
Water	7.1	8.33	---	0.852	---
Aerosol OT (100%)	0.2	9.0**	1.00	0.022	.20
Cellosolve	3.2	7.74	.20	0.414	.64
Water	0.8	8.33	---	0.096	---
	99.0*			9.137	15.36

*"Dowicide" A preservative was not included. Paint made with "Dowicide" B preservative caused agglomeration as it did with the Dupont formula. No antifoam agent was added.

**Figures estimated.

Pigment = 26.8%
Vehicle = 73.2%
Vehicle nonvolatiles = 29.7%
PV = approximately 27.3%
Lbs/gal = approximately 10.85
Viscosity = 78 KU
Ratio of pigment to nonvolatile vehicle solids:
By volume 1 : 2.66
By weight 1 : 0.786
2.61 lbs TiO_2/gal
1.99 lbs Vinac WR-20 solids/gal
5.20 lbs water/gal
Cost = approximately $1.68/gal

Mixing Procedure

1. Add with constant agitation the pigments and fillers to the Methocel.

2. Disperse on 3-roll mill.

3. Dissolve Emulphor EL-719 in water and add to pigment dispersion with constant agitation.

4. Dissolve Aerosol OT in cellosolve and water and add to the pigment dispersion with constant agitation.

5. Vinac WR-20 preplasticized with dibutyl phthalate added with constant agitation.

Observations

Initial viscosity of the paint was 78 KU. After four months storage, the paint is readily redispersed and the viscosity has risen to 90 KU.

The suggested method of preparation resulted in no foaming, but the same method (no antifoam present) using Dupont's Elvacet 81-900 resulted in some foam.

Colton's suggested formula is identical to Dupont's except that no anatase TiO_2 is used and cellosolve is substituted for Carbitol.

Paints made from Vinac WR-20 tend to skin, an inherent characteristic of the resin.

MODIFIED ROHM AND HAAS FORMULA

Ingredient	Percent	Lbs/gal	Cost/lb	Gallons	RMC/100 lbs
TiPure FF	12.5	32.32	0.225	0.387	2.81
TiPure R-610	5.3	34.99	0.245	0.152	1.30
Asbestine XXX	16.5	23.74	0.0175	0.695	.29
Rhoplex AC-33	56.5	8.67	0.265	6.520	14.95
Water	5.1	8.33	---	0.613	---
Acrysol A-3 (10% NH_3salt)	0.5	8.5*	.15*	0.059	.07
Tamol 731 (10% solution)	0.5	8.33*	.15*	0.060	.08
Boric acid	0.6	12.0	0.07	0.050	.04
Diethylene glycol	1.1	9.31	.2025	0.118	.22
Balab 259	0.2	8.50*	.40*	0.235	.08
Ammonium hydroxide 28%	1.2	7.5	.04	0.160	.05
(to pH of 9.0)					
	100.0			8.949	19.89

*Figures estimated.

Pigment = 34.3%
Vehicle = 65.7%
Vehicle nonvolatiles = 42.5%
PV = approximately 30%
Lbs/gal = approximately 11.2
Viscosity = 71 KU
Ratio of pigment to nonvolatile
vehicle solids:
By volume 1 : 2.33
By weight 1 : 0.76
1.99 lbs TiO_2/gal
3.2 lbs AC-33 solids/gal
4.12 lbs water/gal
Cost = $2.22/gal

Mixing Procedure

1. Add Balab 259 to a portion of AC-33 with agitation.

2. Add Tamol 731 and Acrysol A-3 to water with agitation.

3. To a mixture of pigments, extenders and boric acid, add (2) with agitation.

4. To a mixture of (2) and (3), add (1) with agitation.

5. Stir in additional AC-33 to make moist paste. (About 1/2 of total AC-33 used.)

6. Disperse paste by passing through a 3-roll mill. Very little entrapped air.

7. Add remaining AC-33 with agitation. Small agglomerates still remain.

8. Add diethylene glycol and sufficient ammonium hydroxide to a pH of 9.0.

Observations

The AC-33 is very susceptible to foaming. For the most part foaming could be eliminated if the antifoam agent were present in the material being dispersed on a 3-roll mill. Other methods for dispersion were unsatisfactory.

Agglomerates were present in the paint prior to the addition of ammonium hydroxide, which changes the pH from 6.0 to 9.0.

Initial viscosity of the paint was 71 KU. After four months the paint settled a little but was readily redispersed. The viscosity increased slightly to 76 KU.

BAKELITE FORMULA

Ingredient	Percent	Lbs/gal	Cost/lb	Gallons	RMC/100 lbs
TiPure R-510	25.2	34.99	0.245	0.720	6.17
Mica 325 mesh w.g.	2.8	23.49	0.0775	0.119	.22
WC-10*	23.3	see below	see below	2.538	5.54
Cellosize WPHS (5%)	9.3	8.33	0.48	1.117	.22
Ethylene glycol	2.3	9.3	0.1875	0.247	.43
Glyoxal (30%)	0.5	10.48	0.185	0.048	.09
Daxad 11	0.2	---	0.25	---	.05
Tergitol NPX	0.1	8.8	0.315	0.011	.03
Water	36.3	8.33	---	4.360	---
	100.0			9.160	12.75

*Composition of WC-10:

	Lbs	Lbs/gal	Cost/lb	Gallons	RMC
WC-130 latex solids	13.0	9.94	.39	1.31	5.07
Dibutyl Phthalate	1.3	8.75	.3575	0.148	.47
Water	9.0	8.33	---	1.08	---
	23.3			2.538	5.54

Pigment = 28%
Vehicle = 72%
Vehicle nonvolatiles = 21.1%
PV = approximately 36.5%
Lbs/gal = 10.9
Viscosity = 55 KU
Ratio of pigment to nonvolatile vehicle solids:
By volume 1 : 1.74
By weight 1 : 0.51
2.75 lbs TiO_2/gal
1.42 lbs WC-130 solids/gal
4.97 lbs water/gal
Cost = $1.39/gal

Mixing Procedure

1. Dissolve Daxad 11 in water.

2. Add pigments and fillers with agitation.

3. Stir in Cellosize WPHS. Disperse on 3-roll mill or colloid mill.

4. Add WC-10, ethylene glycol, Glyoxal and Tergitol NPX in order with agitation.

Observations

The viscosity of the paint was 55 KU. The finished paint contained large quantities of entrapped air because the Cellosize WPHS was added prior to the pigment dispersion which was then 3-roll milled or run through the colloid mill. Paint settled very badly, although it could be redispersed with sufficient stirring.

The paint contains too much water and/or not enough Cellosize WPHS. Four months aging increased the viscosity to 64 KU.

PIGMENT WATER DEMAND

1% Daxad* 11 solution

Pigment	Fluid paste/100 g**	Comments
OR 540 (TiO_2)	37.2	Paste does not flow
TiPure R-610	46.4	Paste does not flow
TiPure R-510	37.6	Paste does not flow
TiPure R-110	47.8	Paste does not flow
TiPure FF	95.6	(Anatase TiO_2 requires more
TiPure LO	94.4	solution than rutile TiO_2; has slightly better flow
N.J.Z. Kadox 15	95-100	Extremely fluid paste required for removal from spatula, fair flow
N.J.Z. XX505	55.5	Very promising ZnO pigment Fair flow
N.J.Z. XX503	30	Dilatant
E.P. 730	20	Dilatant
E.P. 417	32.5	Dilatant
E.P. 427	42.5	Dilatant
E.P. 415	28	Dilatant
1/2 505; 1/2 503	40	Mixture of dilatant and plastic ZnO was not dilatant but showed fair flow
1/2 505; 1/2 R-510	53	Fluid requirements are not additive
Lorite	66.5	Initial dilatancy good flow; smooth paste
Nytal 300	85	Difficult to disperse; grainy type paste; fair flow
ASP 400	52.5	Excellent flow
ASP 100	71.5	Good flow; no dilatancy
ASP 1100	60.0	Good flow; no dilatancy
Asbestine 3X	62.5	Smooth paste; no flow
Metronite BXXXX	26.4	Slight initial dilatancy Excellent flow
Mica 325	104	Very dilatant
Wollastonite P-1	53.6	Dilatant; poor flow
Wollastonite P-4	47.6	Add additional 5cc promotes good flow but grainy texture
Hydrite	72.0	Smooth paste; fair flow
Hydrite Flat	47.6	Smooth paste; fair flow
Hydrite PD-10	104	Smooth paste that is very fluid but tends to resist flow

*Sodium salts of polymerized alkyl naphthalene sulfonic acids

**Milliliters of solution required to impart sufficient fluidity to the paste so that it will fall from the end of a spatula.

PIGMENT WATER DEMAND (CONT.)

1% solution Igepal* CO-630

Pigment	Fluid paste/100 g	Comments
Metronite BXXXX	36.5	Foams; paste like whipped cream
TiPure R-510	89.0	Foamy paste
Hydrite Flat	86.0	Slightly dilatant
ASP 100	210.0	Very fluid
ASP 400	84.0	Smooth paste
Wollastonite P-4	65.0	Very foamy; appears grainy
E.P. 415	116.0	Very foamy; not dilatant
XX 505	148.5	Foamy; fair flow
Asbestine XXX	90.0	Smooth paste; no flow
Lorite	72.5	Initial dilatancy; foamy paste, fair flow
Nytal 300	100.0	Some entrapped air; fluid paste

1% solution Blancol**

Pigment	Fluid paste/100 g	Comments
Metronite BXXXX	25.5	Slightly dilatant; smooth paste
TiPure R-510	43.5	Poor flow; lumpy paste
Hydrite Flat	49.0	Very dilatant; good flow; smooth paste
ASP 100	68.0	Dilatant; good flow; smooth paste
ASP 400	54.5	Same
Wollastonite P-4	52.5	Very dilatant; not foamy; smooth
E.P. 415	30.0	Very dilatant; excellent flow; smooth
XX 505	66.0	
Asbestine XXX	69.0	Smooth paste; poor flow not dilatant
Lorite	66.5	Initial dilatancy; good flow smooth paste
Nytal 300	84.0	Difficult to disperse; paste appears grainy but it flows

*alkyl aryl polyethylene glycol ether

**sodium salt of condensed naphthalene sulfonic acid

PIGMENT WATER DEMAND (CONT.)

1% solution Nekal* BX-76

Pigment	Fluid paste/100 g	Comments
Metronite BXXXX	34.5	Foamy; like CO-630
TiPure R-510	114.0	Very foamy paste
Hydrite Flat	81.0	Slightly dilatant Like CO-630
ASP 100	145.0	
ASP 400	74.0	
Wollastonite P-4	50.0	Foamy paste; very dilatant
E.P. 415	67.0	Not dilatant; drops clean
XX 505	116.0	Very foamy
Asbestine XXX	96.5	Very foamy
Lorite	68.5	Initial dilatancy; foamy paste; fair flow
Nytal 300	104	Foam; fluid paste

*sodium salt of alkyl naphthalene sulfonic acid plus 20% anhydrous sodium sulfate

SURFACE TENSION*

Wetting Agents	Temperature, °C	Dynes/cm
Distilled water	26	73.3**
1% Nekal BX-76	27	32.6
1% Blancol	27	62.9
1% Igepal CO-630	27	34.0
0.5% Daxad 11	26	72.4-73.2
1% Daxad 11	26	69.5-71.9
2% Daxad 11	26.5	71.3-71.9
1% Darvan 1	26.5	67.8-68.4
1% Darvan 2	26	57.1-53.7
1% Tamol 731	26	51.3-48.7
1% Tamol N	22.5	71.6-72.8
1% Petro AA	29.5	33.5
1% Tergitol NP-35	26	39.9

*Measured on tensiometer C7-6.

**In some instances the values increased or decreased indicating a surface phenomenon. Results appear high since distilled water value should be 71.9.

SURFACE TENSION (CONT.)

Defoaming Agents	Temperature, °C	Dynes/cm
1% Nopco JMY	26	31.6
1% Nopco JMU	26	31.8
DeAirex 506	28	33.9
DeAirex 510	28	34.4
S/V Foamrex S	28	45.4-43.5
AF Paste S-1	28	33.0
Balab 189	28	30.4
Balab 259	28	31.1

Note: The last 3 defoamers and to some extent S/V Foamrex S exhibit poor homogeneity in solution, i.e., a layer rises to the surface. The first 4 defoamers in solution form a homogenous emulsion. S/V Foamrex S solution is like pearl essence.

Mixtures of Wetting Agents and Defoamers	Temperature, °C	Dynes/cm
0.5% JMU - 0.25% Daxad 11	25	44.3-41.0
0.5% JMY - 0.25% Daxad 11	22	31.8
0.5% JMY - 1% Daxad 11	22	40.5-38.2
0.5% JMY - 0.5% Darvan 1	22	42.0-40.6
0.5% JMU - 0.5% Darvan 1	22	44.3
0.5% JMY - 0.5% Nekal BX-76	23	39.2-38.5
0.5% JMU - 0.5% Nekal BX-76	23	39.6
0.5% JMY - 0.5% Tamol 731	23	43.3
0.5% JMU - 0.5% Tamol 731	23	43.3-38.8
0.5% DeAirex 506 - 0.5% Daxad 11	28	41.2-40.5
0.5% DeAirex 510 - 0.5% Daxad 11	28	41.2-40.2
0.5% Petro AA - 0.5% Daxad 11	30	36.5
0.5% Blancol - 0.5% JMY	30	30.8
0.5% Igepal CO-630 - 0.5% JMY	30	35.0
0.5% Tamol N - 0.5% JMY	30	30.8
0.5% Darvan 2 - 0.5% JMY	30	30.4
0.5% Tergitol NP-35 - 0.5% Daxad 11	26	43.4
0.5% Petro AA - 0.5% Darvan 1	30	36.0
0.5% DeAirex 506 - 0.5% Darvan 1	30	37.6
0.5% Balab 259 - 0.5% Darvan 1	30	34.8
0.5% Balab 259 - 0.5% Daxad 11	30	35.6

Note: Blancol and JMY solution has a very active surface.

GLOSSARY

Trade Name	Description	Supplier
Resin Latex		
WC 130	Polyvinyl acetate latex emulsion	Bakelite Company
Elvacet 81-900	Polyvinyl acetate latex emulsion	Dupont Company
Vinac WR-20	Polyvinyl acetate latex emulsion	Colton Chemical Co.
Shawinigan TS-22	Polyvinyl acetate latex emulsion	Shawinigan Products
Resyn 12K51	Polyvinyl acetate latex emulsion	National Starch Co.
Everflex G	Polyvinyl acetate latex emulsion	Dewey and Almy Co.
Rhoplex AC-33	Acrylic resin emulsion	Rohm and Haas Co.
Thickeners		
Acrysol GS	Sodium polyacrylate	Rohm and Haas Co.
Acrysol A-3	Polyacrylic acid	Rohm and Haas Co.
K-707	Ammonium polyacrylate	B. F. Goodrich Chem.Co.
Cellosize WPHS	Hydroxyethyl cellulose	Carbide and Carbon
Cellosize WP-300	Hydroxyethyl cellulose	Carbide and Carbon
CMC	Carboxymethyl cellulose	Hercules Powder Co.
Methocel	Methyl cellulose	Dow Chemical Co.
Pigments		
TiPure R-110	Titanium dioxide (rutile)	Dupont Company
TiPure R-510	Titanium dioxide (rutile)	Dupont Company
TiPure R-610	Titanium dioxide (rutile)	Dupont Company
TiPure FF, LO	Titanium dioxide (anatase)	Dupont Company
Unitane OR 540	Titanium dioxide (rutile)	American Cyanamid Co.
Kadox 15	Zinc oxide	New Jersey Zinc, Inc.
XX505, XX503	Zinc oxide	New Jersey Zinc, Inc.
E.P. 415, 417, 427, 730	Zinc oxide	Eagle Picher Co.
Fillers		
ASP 100, 400, 1100	Aluminum silicate	Edgar Bros., Inc.
Metronite BXXXX	Calcium magnesium silicates and carbonates	MetroNite Company
Mica 325 w.g.	Mica	English Mica Co.
Asbestine 3X	Magnesium silicate	International Talc
Nytal 300	Magnesium silicate	R. T. Vanderbilt Co.
Wollastonite P-1	Calcium silicate	Godfrey L. Cabot, Inc.
Wollastonite P-4	Calcium silicate	Godfrey L. Cabot, Inc.
Hydrite and Hydrite PD-10	Hydrated aluminum silicate	Georgia Kaolin Co.
Hydrite Flat	Hydrated aluminum silicate	Georgia Kaolin Co.
Lorite	Calcium carbonate; diatomeacous silica	National Lead Co.

Trade Name	Description	Supplier
Dispersing and Wetting Agents		
Emulphor EL-719	Polyoxyethylated vegetable oil	General Dyestuff Corp.
Aerosol OT		American Cyanamid Co.
Tergitol NPX	Alkyl phenyl ether of polyethylene glycol	Carbide and Carbon
Tergitol NP-35	Alkyl phenyl ether of polyethylene glycol	Carbide and Carbon
Daxad 11	Sodium salts of polymerized alkyl naphthalene sulfonic acids	Dewey and Almy Co.
Blancol	Sodium salt condensed naphthalene sulfonic acid	General Dyestuff Corp.
Nekal BX-76	Sodium alkylnaphthalene sulfonate	General Dyestuff Corp.
Igepal CO- 630	Alkyl phenoxy polyoxyethylene ethanol	General Dyestuff Corp.
Tamol 731		Rohm and Haas Co.
Tamol N		Rohm and Haas Co.
Darvan 1	Polymerized sodium salts of alkylnaphthalene sulfonic acids	R. T. Vanderbilt Co.
Darvan 2	Polymerized sodium salts of subsituted benzoid alkylsulfonic acids	R. T. Vanderbilt Co.
Petro AA	Alkyl aryl sodium sulfonate	Petrochemicals Co.
Defoamers		
JMY		Nopco Chemical Co.
JMU		Nopco Chemical Co.
DeAirex 506		E. F. Houghton and Co.
DeAirex 510		E. F. Houghton and Co.
S/V Foamrex S		Socony Vacuum Co.
AF Paste S-1		Polymer Southern Inc.
Balab 189		Balab Co.
Balab 259		Balab Co.
Miscellaneous		
Carbitol	Diethylene glycol monoethyl ether	Carbide and Carbon
Cellosolve	Ethylene glycol monoethyl ether	Carbide and Carbon
Glyoxal	Glyoxal	Carbide and Carbon