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NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

TITLE: PIGMENT DISPERSION IN POLIVINYL ACETATE LATEX PAINT.

Period Covered

JULY - OCTOBER, 1954

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

PROGRESS REPORT

TITLE: PIGMENT DISPERSION IN POLYVINYL ACETATE LATEX PAINT.

PERIOD COVERED: JULY, 1954 - OCTOBER, 1954.

CHARGE: A-IIC-321

SUBMITTED BY: F. F. EHRICH DATE SUBMITTED: 11/15/54

APPROVED BY: A. A. BRIZZOLARA DATE ISSUED:

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INTRODUCTION:

Until recently, the major emphasis in the latex paint field has been on the "rubber-base" paints based on plasticized polystyrene and styrene-butadiene copolymers. Latex paints based on polyvinyl acetate or polyacrylate water-dispersions are now increasing in importance, particularly for exterior paint use.

The problem of pigment dispersion has proven to be somewhat of a drawback in the application of polyvinyl acetate (PVA) for latex paints. The dispersion considerations are complicated by the fact that optimum pigment dispersion must be effected at a pH lower than that prevalent in the rubber-base or polyacrylate paint systems. The latter systems are distinctly on the alkaline side and unlike polyvinyl acetate systems, do not experience a pH drift downward.

Whereas our current line of anionically dispersed pastes is not completely unsatisfactory in PVA systems, e.g., GW-749-P, YW-672-P, YW-613-P, YW-694-P, at least two and possible three items viz. BW-372-P, RW-704-P, and RW-706-P are particularly bad with respect to flocculation in such systems. Accordingly, this work was undertaken to determine the critical factors involved in pigment dispersion in polyvinyl acetate systems and to develop a suitable line of dispersible colors for use in these paint systems.

SUMMARY AND CONCLUSIONS:

A complete line of pigment colors, tentatively selected on the basis of durability as being suitable for use in exterior paint applications has been modified by surface treatment with selected non-ionic agents to facilitate their dispersion in polyvinyl acetate paint systems. It has been further demonstrated that such non-ionically dispersed colors will perform satisfactorily in typical butadiene-styrene systems, and in acrylic paint systems.

There is evidence that the presence of suitable non-ionic protective colloids, present either in the dispersed pigment paste or in the paint formulation, will further stabilize the pigment dispersion.

A practical plant process for the manufacture of non-ionically dispersed pigment pastes has not been developed in this work. Rather, a principle has been demonstrated which should enable the development of a complete line of non-ionically dispersed pastes for general use in water emulsion paint systems including polyvinyl acetate, butadiene-styrene, and the acrylics.

DISCUSSION OF RESULTS:

Poor pigment dispersion in polyvinyl acetate emulsion paints is evidenced by the increased color strength obtained when the wet,

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tacky paint film is vigorously finger-rubbed to dryness. Several possible mechanisms of pigment flocculation were investigated:

1) Pigment migration into the dibutyl phthalate which serves as a non-solvent plasticizer for polyvinyl acetate.

A CPC toner paste (N-623) was flushed into dibutyl phthalate and this was then used to tint a typical exterior white formulation (Newport W-8). Poor strength and severe flocculation versus a control were obtained.

2) The possibility of poor wetting and poor dispersion of the pigment in the methyl cellulose which serves as a paint thickner and protective colloid in the formulation. BW-372-P disperses very poorly into a methyl cellulose gel (2% 4000 cps) such as is used in the paint formulation. When 3.2 parts of methyl cellulose were gelled in the presence of 200 parts of BW-372-P (no additional water added) and the blue gel so formed used to tint a white formulation, poor strength and severe flocculation versus a control were observed. Either the methyl cellulose is not completely dispersed within the paint system or the pigment, though originally well water-dispersed as BW-372-P, is "flocculated" within the methyl cellulose gel in this concentrated medium.

Attempts to disperse TiO_2 together with BW-372-P in Methocel by gelling the latter in the presence of the blue and white pigments offered no advantage over a control.

Substitution of casein for Methocel in a tint base formulation did not offer any advantage with respect to pigment flocculation. However, when BW-372-P was dispersed in a relatively large amount of water and the diluted dispersion subsequently gelled with methyl cellulose, a good pigment dispersion was obtained in the paint formulation as evidenced by a relatively small amount of "flocculation". The use of a non-ionic surface agent (water-insoluble Tergitol NP-14) in the paint formulation in conjunction with the above variation gave evidence of still greater pigment strength.

3) Treatment of BW-372-P (Daxad-dispersed CPC Blue) with a series of non-ionic surface active products of different hydrophyllic-hydrophobic balance showed some evidence that the water-insoluble members of the series were the more effective in minimizing pigment "flocculation" (Tergitol NP-14, Igepal CO-430, CO-530). Presumably, the latter modify the hydrophyllic character of the Daxad or serve, possibly, as protective colloids.

4) Pigment incompatibility with polyvinyl acetate due to coating of the latter with water-soluble polyvinyl alcohol used as a protective colloid for the PVA: Much as polyvinyl alcohol is used in the production of resists to prevent dyes from adhering to fabrics, the possibility that it prevents the adherence of organic pigments to polyvinyl acetate was

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considered.

5) Pigment flocculation resulting from the relatively low pH's of polyvinyl acetate systems.

Whereas a technique has been devised which assures fair dispersion of BW-372-P in a methyl cellulose gel with a consequent improvement in dispersion in a polyvinyl acetate paint system, optimum dispersion is not achieved in this manner. It is speculated that the non-ionic methyl cellulose serves as a protective colloid for the anionically dispersed CPC pigment, and preserves its state of dispersion in the acidic polyvinyl acetate paint system.

CPC Blue (N-623) was dispersed in the recommended exterior white PVA paint formulation (W-8) employing Elvacet 81-900 PVA emulsion, to give products essentially free of flocculation as shown by the finger rub test. Freedom from flocculation is further evident in greater color strength. Other paint properties have not been evaluated. N-623 (aqueous paste of solvent-ground LB/CPC) was treated with two series of non-ionic surfactants (8 Igepals and 5 Tergitols), successive members of which have a different hydrophyllic-hydrophobic balance. An essentially orderly increase in dispersion is obtained as evidenced by paint strength and freedom from flocculation. Igepal CO-610 and CO-630, and Tergitol NP-27 and NPX yield the best paints. The above agents are adjacent to each other within their respective series and all are in the same range of hydrophyllicity. The best products are superior to those obtained using BW-372-P (Daxad dispersed CPC Blue) as the color source, or versus an absolute control using Daxad as the dispersing agent. The latter gives a product fully equal to BW-372-P which confirms its value as a control. It is significant that the most effective agents in these series are not the most hydrophyllic. In an arbitrary range of hydrophyllicity from 43 to 81, the most effective agents for this application are in the region 61 to 63.

A variety of other surface-active agents have been tested and several have been found to be equal or superior to BW-372-P (or a Daxad control) although not equal to the best acting Tergitols or Igepals. (Emulphor EL-719, Sterox CD, Tamol 731, and Triton X-100). Ammonium caseinate yielded a product essentially equal to the best.

The technique described above with reference to the optimum non-ionic dispersion of CPC was applied to a complete line of pigment colors, tentatively selected on the basis of durability as being suitable for use in exterior paint applications. These colors were modified by surface treatment to facilitate their dispersion in polyvinyl acetate paint systems. The respective toner pastes were treated by ball milling with two series of non-ionic surfactants, the successive members of which have a different hydrophilic-hydrophobic balance. An orderly

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progression of dispersion was observed. Optimum dispersion is evidenced by freedom from flocculation (finger rub test) and greater pigment strength. In addition to the non-ionic agents, ammonium caseinate, and Daxad 11KLS (anionic agent) were included in each series. The latter was used so as to confirm the behavior of the current line of dispersed pastes which are prepared for the most part by the use of analogous surface agents. In all cases, evaluation was made in the Newport-recommended W-8 exterior white formulation which incorporates du Pont's Elvacet 81-900 PVA emulsion. Paint properties other than strength or flocculation resistance were not evaluated. The results are tabulated in Table I. All of the dispersed pastes described contain approximately 15-20% pigment toner, and 25% of surface agent based on the toner present. The agents were incorporated by milling with the toner paste for 72 hours in a 1/2 pt. glass jar containing glass beads. To determine the effectiveness of homogenization (in lieu of milling) for the purpose of incorporating the surface agent, Green GK paste (N-764) was homogenized (one minute recirculation at 5,000 psi, SW unit) with 5, 15 and 25% amounts of Igepal CO-530 and CO-610, respectively. The 25% products were superior strengthwise, although equal flocculationwise, to the 72 hour milled controls. Increased strength and flocculation resistance was evident with the higher amounts of agent.

Initial attempts to prepare a TiO_2 white dispersion using non-ionic agents exclusively yielded products slightly superior to the W-8 exterior white control.

Excellent dispersion of non-ionically dispersed CPC was obtained in the Litter Laboratories white formulation, which uses Polyco's polyvinyl acetate emulsion and which employs non-ionic dispersants for the white. The W-8 formulation uses both anionic and non-ionic dispersants.

Non-ionically dispersed CPC Blue yielded a wholly non-flocculating tint in a typical Dow butadiene-styrene latex formulation and in a typical acrylic emulsion paint formulation. The flocculation-resistance was at least equal to that observed with the present dispersed paste for latex paint, BW-372-P.

There is some evidence that anionically treated colors, (BW-372-P, YT-674-P, YT-580-P) can be rendered more effective, dispersion-wise, in a PVA system by applying a protective colloid or water-insoluble surface active agent (e.g. Methocel, Igepal CO-430, Tergitol NP-14). In either case, a protective coating is applied to the anionically dispersed color which renders it, at least temporarily, immune to the effects of the acidic polyvinyl acetate system. The very effective action of ammonium caseinate presumably arises from its dual roll as pigment dispersant and protective colloid. Ammonium caseinate should

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TABLE I.

	Exp't No.	Starting Toner Paste	Preferred Agent(s)	Freedom from Flocculation in W-8 Exterior White
CPC Blue	1514-14	N-623	Igepal CO-610	Excellent -
			Tergitol NP-27	"
			NH_4 Caseinate	"
CPC Green GX	1514-15	N-764	Igepal CO-530, CO-610	Good +
			Tergitol NP-27	"
			NH_4 Caseinate	"
Hansa Yellow G	1514-17	YT-574-P (High blancol in coupling)	Igepal CO-530, CO-610	Excellent -
			Tergitol NP-27	"
			NH_4 Caseinate	"
Hansa Yellow G	1514-24	YT-580-P (low blancol in coupling)	Igepal CO-530, CO-610	Excellent -
			Tergitol NP-27	"
			NH_4 Caseinate	"
Green Gold	1514-18	YT-675-P	Igepal CO-610, CO-630	Excellent
			Tergitol NP-27, NPX, NH_4 Caseinate	"
Hansa Yellow 10G	1514-22	YT-85-P	Igepal CO-610	Excellent
			NH_4 Caseinate	"
Para Chlor Red	1514-23	RT-598-P	Igepal CO-610	Excellent -
			Tergitol NP-27	"

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prove to be an excellent dispersant in a buffered PVA or other latex systems as should the use of a protective colloid (or less water-soluble surface agents, e.g. Tergitol NP-14, Igepal CO-430, etc.) in conjunction with the recommended non-ionic dispersants.

As has been intimated previously, the most effective non-ionic agents for pigment dispersion in PVA systems are not the most hydrophilic but rather those which exhibit a limited solubility in the system. Under the latter condition, the agent presumably migrates to an interface and facilitates micelle formation.

NOTEBOOK REFERENCE:

NB-1514

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APPENDIX I.

NEWPORT W-8 EXTERIOR WHITE FORMULATION

Ingredients	Lb./100 Gal.
3-Roll Mill Base	
"TiPure" R-610	246.0
Mica. 325 Mesh Waterground	41.0
2% Methocel 4000 cp. Solution	163.5
Polyglycol P-1200	2.0
Tamol 731 - 10% solution	12.2
Reduction	
(a) Water	176.7
Emulphor EL-719 (1)	2.2
(b) Ethyl Carbitol	34.3
Water	8.8
20% Dowicide A solution	11.5
(c) "Elvacet" 81-900	356.0
Dibutyl Phthalate	29.0
	1083.2

(a), (b), (c) premixed solutions
(1) Previously designated Emulphor ELA

Initial Consistency (KU): 76
Gallon Weight (actual): 10.83
PVC: 27%

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APPENDIX II.

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PIGMENTS DEPARTMENT

cc; J. E. Booge/I. J. Krchma
D. B. Killian, Wilmington
J. A. Fredrickson, "
J. N. Tully/A. Siegel
W. F. Spengeman/O. F. Lane
A. A. Brizzolara
Pigments-Wilmington File

NEWARK, NEW JERSEY
AUGUST 9, 1954

MEMORANDUM FOR FILE

PIGMENT DISPERSION IN POLYVINYL ACETATE EMULSIONS

Report of visit to the Electrochemical's Department, Niagara Falls, N. Y., with O. F. Lane, August 3, 1954.

PURPOSE:

To acquaint the writer with the nature of polyvinyl acetate emulsion paint systems, the mechanism of pigmented film formation, and the experiences of Elchem in their efforts to prevent the apparent flocculation of pigment colors in such systems.

PERSONS INTERVIEWED:

R. D. Emmick
D. A. Swalheim

Polyvinyl acetate emulsion paint films form by coalescence of the plasticized PVA particles as a consequence of water evaporation. The film forms by collapse so that, for the most part, the polyvinyl acetate and the other paint constituents retain the same relative positions in the dried film as in the wet emulsion paint. To minimize pigment flocculation in the final film, therefore, it is necessary to effect the optimum dispersion of the pigments, both white and colored, in the emulsion paint system.

Photomicrographs of the original paints and semi-dry and dry paint films indicated that flocculation of the white pigment is a condition present in the original paint and no additional flocculation occurs on drying. Rubbing the semi-dry film gives better dispersion of the white by breaking up the flocs. If the colored pigment is held inside the white pigment flocs, such rubbing treatment would release it from the hiding white pigment and thus give a darker color. Electron-micrographs of paint films deposited from paints diluted 1 to 25 with water indicated that the titanium dioxide was flocculated and in each case it was flocculated around the polyvinyl acetate particles. In

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some instances, only a portion of the floc was in direct contact with the PVA particle. These results indicate the need either for better initial dispersion of the white pigment or, if the initial dispersion is adequate, modifiers which will prevent the flocculation of the white pigment as the other paint ingredients are added.

Elchem has investigated the use of surface active agents rather extensively (Progress Report - Elchem NF-54-81) in attempts to find a completely satisfactory solution to the problem of flocculation of colored organic pigments in light tints and conclude that improvement in this respect will probably have to come from variations or improvements in the method of preparation of the paints with their present Elvacet 81-900 vehicle. The latter was originally developed for use as an adhesive rather than as a paint vehicle.

Elchem is currently developing a PVA vehicle for paint use which incorporates a polyvinyl acetate of smaller particle size. Initial evaluations show such formulations to be superior with respect to water resistance, and pigment flocculation tendencies as compared to the present vehicles.

F. F. EHRICH
CHEMICAL DIVISION

jc

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APPENDIX III.

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J. N. Tully/A. Siegel
A. A. Brissolara
D. B. Killian, Wilmington
Pigments-Wilmington File
W. F. Spengeman/O. F. Lane

NEWARK, NEW JERSEY
NOVEMBER 12, 1954

MR. J. A. FREDRICKSON
WILMINGTON

PIGMENT DISPERSION IN POLYVINYL ACETATE SYSTEMS

As per your request, we are listing below the non-ionic surface-active agents which were found to be effective in dispersing pigment colors in polyvinyl acetate paint systems. We understand that attempts will be made to substitute such agents for the anionic agent currently used in the W-8 exterior white formulation.

Igepal CO-610
Igepal CO-630
Tergitol NP-27
Tergitol NPX

The preferred agents are Igepal CO-610 (Antara Chemicals Division, General Dyestuffs Corp.) and Tergitol NP-27 (Carbide and Carbon Corp.).

The possibility that one such agent can displace both the Emulphor and the Tamol in the W-8 formulation is suggested.

It might be of interest to investigate the entire homologous Igepal series (8 members) or the Tergitol series (5 members) so as to determine the organophilic-hydrophilic balance required for optimum dispersion. The work with pigment colors showed an essentially orderly progression of dispersion with a maximum dispersion shown by the Igepal CO-610.

F. F. EHRICH
CHEMICAL DIVISION

jc

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