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E. I. du Pont de Nemours & Company

F & F, Research & Development Division

Experimental Station Laboratory

Research Report

PIGMENT DISPERSION
COMMERCIAL POTENTIAL OF A-B DISPERSANTS

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TABLE OF CONTENTS

INTRODUCTION

A program to utilize the concepts of Entropic repulsion, in developing deflocculated pigment dispersions, has been in progress at this laboratory for several years (1, 2, 3, 4, 5, 6, 7).

Until recently, the flocculation stability of pigmented dispersion made using A-B* type polymeric dispersants was very sensitive to highly polar solvents and to polymers present in most major film forming systems. Recently developed A-B dispersants have provided deflocculated pigment dispersions which function satisfactorily in several commercial film forming systems.

The current program is designed to establish the commercial potential of selected A-B dispersants by defining their performance in selected new product developments.

OBJECTIVES

The overall program objective is to provide a simplified high quality mill base system based on A-B type polymeric dispersants.

The immediate program objective is to define the commercial potential of specific A-B dispersants in selected new product systems; namely, acrylic organosol automotive lacquers and LBA urethane enamels.

The acrylic organosol program is our top priority product system at this time. The program work is designed to show the advantages of deflocculated mill bases in the product system and to establish that the A-B dispersants do not adversely effect other film or product properties.

*A-B polymeric dispersants are specifically designed to provide flocculation stability for dispersed pigment particles in an organic medium. The "A" segment of the molecule is designed for strong adsorption on pigment while the "B" segment of the molecule is designed to provide a solvated polymeric environment around the pigment particle.

SUMMARY AND CONCLUSIONS

Recently developed A-B type polymeric dispersants are capable of providing deflocculated pigment dispersions which remain deflocculated when let down into commercial film forming systems. Deflocculated films of dispersions made with A-B dispersants have been made in:

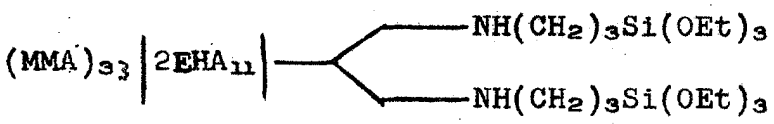
A. Alkyd and modified alkyd products

B. Acrylic (solution and organosol form) products

C. Acrylic modified urethane products

I. The L.B.A. Urethane Enamel Product System

Deflocculated mill bases were formulated for W-74 (TiO_2), W-686 (Chrome Yellow), W-819 (Quinacrdone red), W-765 (Monastral® green), W-577 (Monastral®blue), W-608 (Yellow Ni-TiO_2 Complex), and W-362 (Red Iron Oxide). The dispersions for W-74, W-686, and W-819 were scaled-up to the 1/2 gallon continuous feed "47P" unit and two gallons of each dispersion was sent to the Marshall Laboratory for more extensive comparative evaluation of their performance in the L.B.A. urethane product system. These dispersions used a silane type A-B dispersant which has the following structure:



II. Automative Acrylic Organosol Product System

A formulating technique is being established for compounding organosol products so that effective evaluation of A-B dispersant mill bases can be obtained. Initial results show that deflocculated dispersions can be made with A-B dispersants for use in the acrylic organosol product. These dispersions can be made with and without solution form organosol polymer. The use of the solution form organosol polymer is primarily, to control mill base viscosity, if it is needed to permit efficient mill base manufacture and processing.

Mild flocculation of the dispersed pigment is encountered during the let down into finished product formulation and also during film formation. The flocculation is believed due to the solubility and compatibility of the A-B dispersant with solvent system during let down and to the compatability of the A-B dispersant with the polymer phases during film formation. However, the quality of the final film is still quite good, showing good color development and transparency. Prototype formulations for both product compounding and mill bases are being sent to Flint for further evaluation. Initial results with product compounding indicate a revised solvent system and specific order of addition may provide a high solids product (26-30% vol. solids) with the required stability.

III. Acrylic Modified PVF Coil Coating Product System

Work begun in this product system early in the report period has been discontinued. Initial results indicated that the acrylic "B" segment of the silane type A-B dispersant

$$[(MMA_{33}\ 2EHA_{11}\text{—}\begin{matrix}\text{silane}\\\text{silane}\end{matrix})]$$

needed to be modified to improve the compatability of the dispersant with the product vehicle and solvent system. Further work has been postponed.

IV. During this report period the acrylic organosol product system and the acrylic modified polyurethane product system were selected as the two top priority areas for this program effort.

ACTION TAKEN OR PROPOSED

Efforts will continue to establish commercial potential of A-B dispersants in the acrylic organosol product system. Development of mill base formulations that are compatible with the overall production of an organosol automotive finish will be continued in cooperation with Flint and Marshall Lab personnel. Data will be obtained to determine what measurable effects A-B dispersants have on major film and product properties such as durability, cold crack resistance, Cleveland Humidity whitening, etc.

Additional work on dispersions for the L.B.A. urethane system has been postponed until we have some data back on the effect of A-B dispersants on durability and other properties.

PATENT STATUS

The patent situation concerning the A-B dispersants is covered in ESR-69-52. No patent action is contemplated on the contents of this report.

PUBLICATION STATUS

Publication of this work is not anticipated.

ACKNOWLEDGMENTS

The writer wishes to acknowledge helpful discussions with F. N. Jones and I. C. Chu concerning A-B dispersants and their performance, to W. S. Bullock, Flint Lab, and to L. A. Becton, Marshall Lab for valuable assistance on the acrylic organosol product system, and to G. G. Sun and D. R. Strehlau, Marshall Lab, for assistance on the L.B.A. urethane system. Also, to acknowledge the diligence and conscientious effort of R. A. Lambert in executing most of the laboratory work.

DISCUSSION

Early in this report period, after evaluating the many possible routes to commercialize A-B dispersants and discussing possible routes with production, sales, and research personnel, the L.B.A. urethane enamel and the acrylic organosol product systems were selected. The two product systems selected represent both new technology and new product developments of large potential in both enamel and lacquer product systems.

I. L.B.A. Urethane Product System

The L.B.A. product system has two major film forming components, RC-66047 which is a

Styrene/MMA/HEA/-Phthal. Anh./Cordura E
29.5 /15/16.5/ 14 / 25

(containing hydroxyl and some acid functionality) and Desmodur "N", a tri-functional isocyanate. The RC-66047 is a good dispersing polymer for some pigments such as TiO_2 and iron oxide. The RC-66047 is not as efficient or effective as several A-B type dispersants in dispersing and deflocculating pigments.

From several satisfactory A-B type polymeric dispersants, the

$MMA_{33} | 2EHA_{11}$ — silane dispersant / silane dispersant

was chosen because it worked with a wide range of pigments, was available in large quantities, and is being used in the acrylic organosol program. The MMA| 2EHA "B" segment is used with the following "A" groups:

1. Acid "A" group $-[SCH(CH_2COOH)COOH]$
2. Silane "A" group $[NH(CH_2)_3Si(OEt)_3]_{2/3}$
3. Mixed-Silane-Amine "A" group $[NH(CH_2)Si(OEt)_3]_{2/3}$ / $[NH(CH_2)_2N(ME)_3]_{1/3}$
   $_{2/3}$ to $_{1/3}$ respectively

These dispersants should provide the capability of a complete pigment gamut with excellent deflocculation of the pigment. Well deflocculated dispersions were made using A-B dispersants for TiO_2, Chrome yellow, Monastral® Red, Red Iron Oxide, Phthalo Blue and Green. (Formulations for each of the dispersions are

contained in the Appendix, Section I.) Evaluation of each of the above dispersions in the L.B.A. product showed superior color development and excellent gloss and appearance when compared with control dispersions dispersed in RC-66047.

Dispersions of TiO_2 (W-74), Chrome yellow (W-686), and Monastral Red (W-819) were scaled up to a 1/2 gallon continuous "47P" unit. Each of the dispersions processed satisfactorily. The TiO_2 dispersion was slightly thixotropic which was not indicated in the "47 P" beaker grinds. A slight modification in the level of A-B dispersant (0.1 to 0.25% increase) is expected to eliminate the problem. The dispersion for the W-819 (monastral red) was also thixotropic at 20% pigment. Reduction to 15% pigment with additional solvent eliminated the thixotropy. Samples of each of the scaled up dispersions were supplied to the Marshall Laboratory for evaluation to determine the effects of these dispersions on film and product properties.

Each of the dispersions were also evaluated in other vehicle systems. The dispersions provided excellent deflocculation of the pigment in Alkyd, melamine, and some acrylic polymer and vehicle systems. This data indicates possible use of this type of dispersion in other product systems such as 93 Line, 195 Line, 180 Line, 780 Line, 752 Line, etc. However, the solvent system used in the dispersions (H-735-moisture free cellosolve acetate) was chosen for the L.B.A. system only. A compromise in the mill base solvent would be possible if sufficient justification was shown for reformulating existing product systems.

II. Automotive Acrylic Organosol Product System

F. N. Jones has selected 3 A-B type dispersants for use in developing pigmented dispersions for the acrylic organosol product system. Each of the dispersants uses the same "B" segment, i.e. $MMA_{33} \mid 2EHA_{11} \mid$. The three (3) "A" segments are silane, acid, and $_{2/3}$ silane-$_{1/3}$ amine in functionality.

The silane type A-B dispersant has been used to prepare pigmented dispersions of TiO_2 (W-74), Monastral Red

(W-819 and W-839), Chrome yellow (W-686). Dispersions of other pigments have been made by F. N. Jones and I. C. Chu and are reported separately.

Most of the work in this report period on the acrylic organosol phase of the program has been with W-839 (Monastral Red). This work has been pursued in three related but separate phases: Mill base formulation using A-B dispersants, product compounding for effective evaluation of mill base quality, and product compounding in terms of viscosity and rheological stability at high product solids.

Two mill base formulations have been developed for W-839 (see Appendix, Section II). Each formulation contains a solvent blend, the silane A-B dispersant and pigment. One of the formulations also contains a solution form of the organosol polymer (9470-5). The solution form polymer 9470-5 is an older self-stabilized polymer form which showed moderately good wetting properties for some pigments (TiO_2, Phthalo Green). It is expected that other solution form polymers would function as well. The solution form polymer is used to increase the mill base viscosity, to improve milling efficiency in the "47P" unit, and to provide improved processing and handling capability in plant equipment. Microscopic examination of the two dispersions does show improved grinding efficiency with the solution form polymer in the mill base.

Each of the above dispersions are well deflocculated. When let down into the product system, some mild flocculation of the dispersion does take place. The degree of flocculation can be effected by orders of addition in product compounding. (See Appendix, Section II, for recommended formulation.) The flocculation encountered on let down and during film formation is not severe and is expected to provide more than adequate product quality.

The flocculation encountered is believed due to
1. the multiphase nature of the polymer in the dry film and
2. the mutually antagonistic requirements for the dispersant in this vehicle system i.e. tolerance to aliphatic solvents and compatability with the organosol polymer.

A tentative procedure for let down of the mill base into a product is to add the two plasticizers to the organosol polymer with some xylene and mix 1/2 hour. At this point, the plasticizers and the xylene will solvate some additional organosol polymer. The viscosity increase is slight and well within production equipment capability. The added polymer in solution aids in coating the pigment particles and tends to protect them against flocculation when the non-solvent, Isopar-E, is added slowly as the last ingredient. (See Appendix, Section II for formula details.) It should be noted that additional data are required with several pigments and pigment to binder ratios to finalize the above procedure.

A tentative formulation technique is also presented as a possible route to a high solids product make-up. Sufficient data are not yet available to insure capability but initial viscosity stability at ambient and elevated (140°F) temperatures is promising (see Appendix, Section II, for formulation details and viscosity data).

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5. Thompson, D. R. ESR-66-54

6. Thompson, D. R. ESR-67-51

7. Ashe, T. A. ESR-68-26

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SAMPLE 424E-163 A

VOLUME SOLIDS = 26.5%

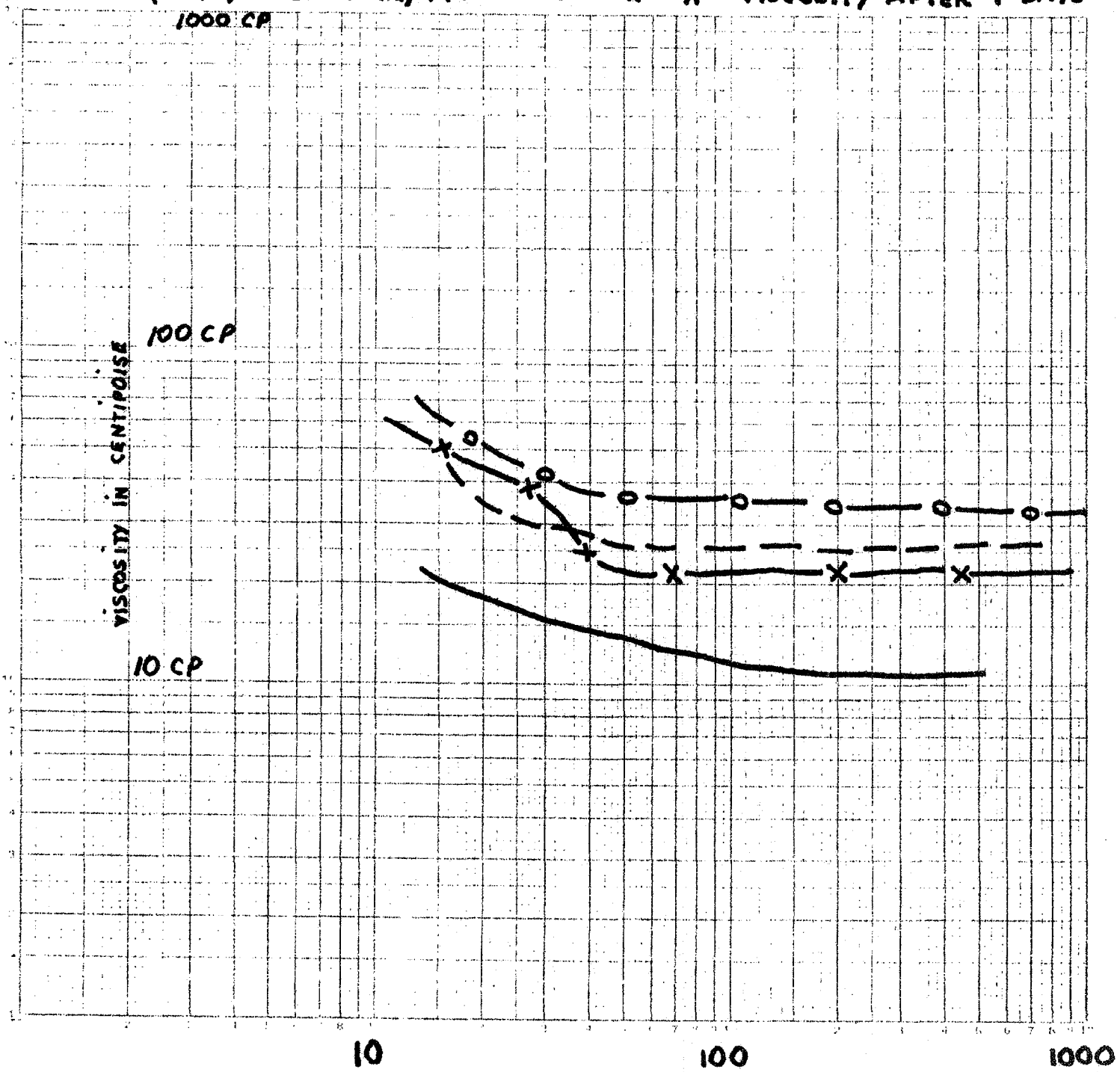
LEGAND

——————— INITIAL VISCOSITY

— — — — — 140°F VISCOSITY AFTER 4 DAYS

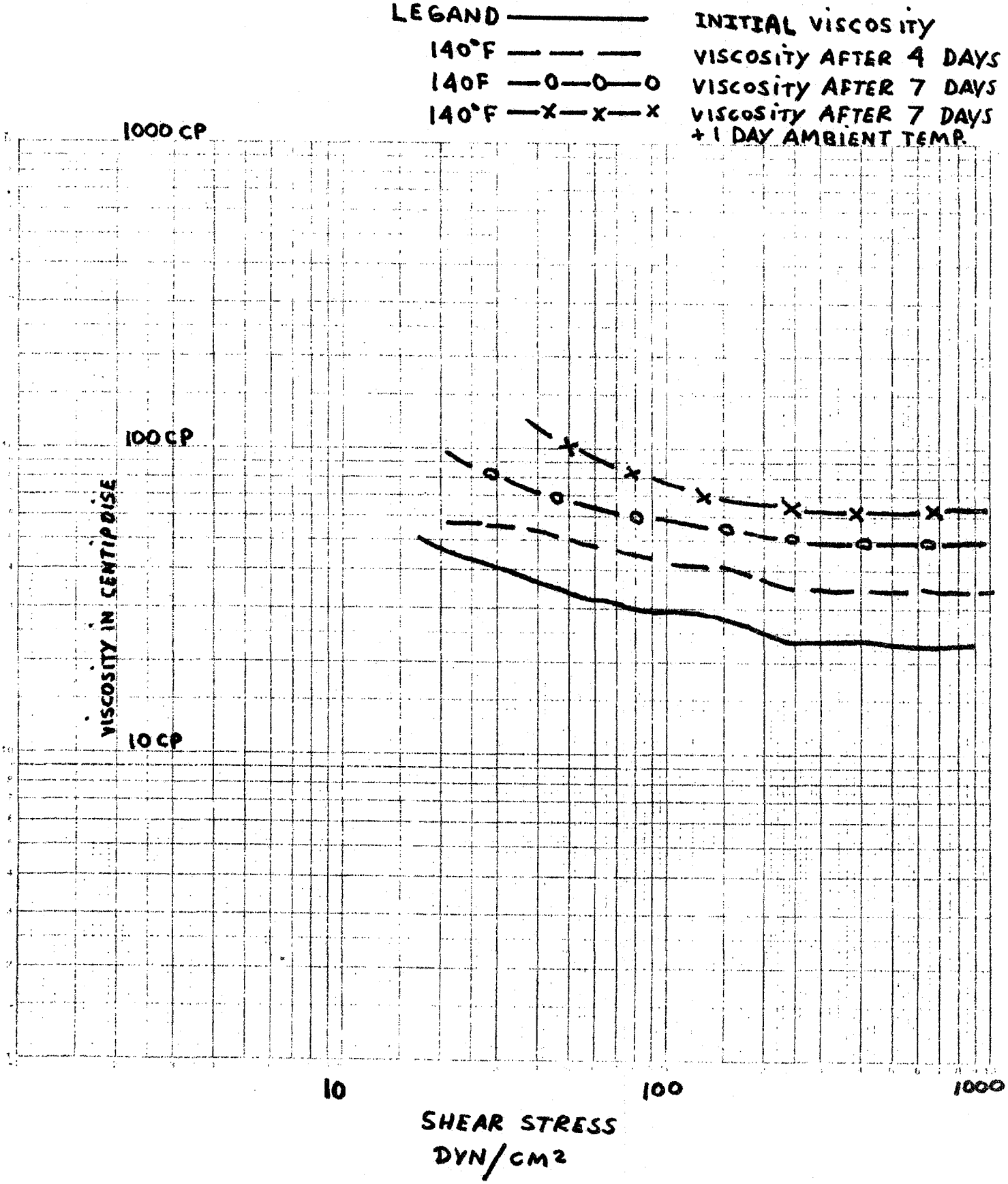
—o—o—o— 140°F VISCOSITY AFTER 7 DAYS

—x—x—x— (+1 DAY AMBIENT TEMP) 140°F VISCOSITY AFTER 7 DAYS



SAMPLE 424E-163 B

VOLUME SOLIDS = 27.5%



SAMPLE 424E-163C

VOLUME SOLIDS = 30.5%

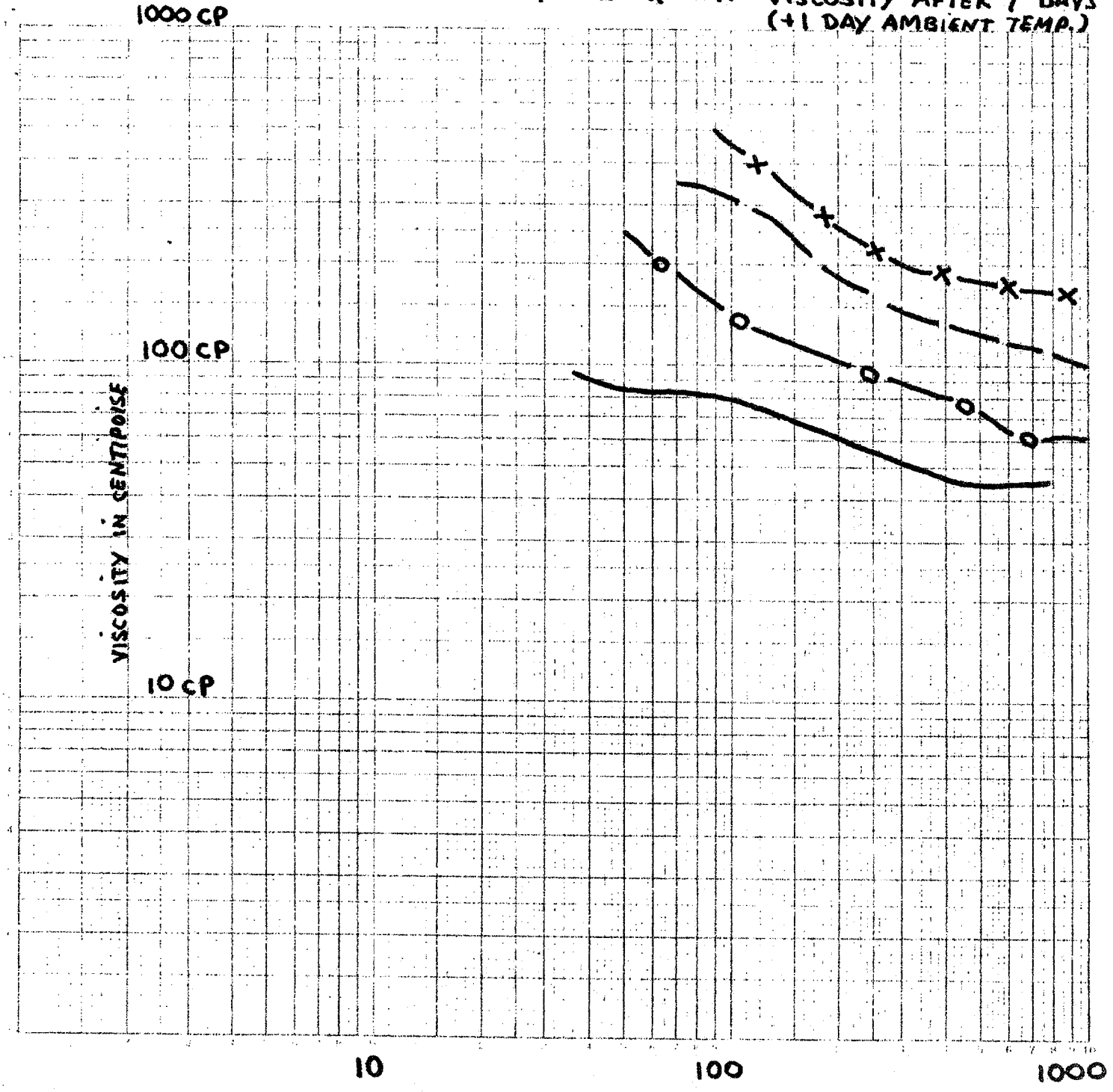
LEGAND

———— INITIAL VISCOSITY

140°F - - - - - - VISCOSITY AFTER 4 DAYS

140°F —o—o—o VISCOSITY AFTER 7 DAYS

140°F —x—x—x VISCOSITY AFTER 7 DAYS (+1 DAY AMBIENT TEMP.)



APPENDIX, SECTION I

L.B.A. URETHANE PRODUCT - MILL BASE FORMULATION

Code	%		Remark:
H-735	34.0	(Cellosolve acetate)	Add in order with mixing Mix 1/2 hour after all TiO_2 is in Grind "47P" 50/50 sand/base 6 min. stay time
448E-104	1.0	(Silane Dispersant)	
W-74	65.0	(TiO_2 R-960)	
	100.0		

H-735	33.75		Instructions same as above.
448-E-104	1.25		
W-686	65.00	(Chrome yellow)	
	100.00		

The level of A-B dispersant was chosen to minimize settling via beaker type formulations some modification of dispersant level may be required on scale-up to retain desired properties. If the use of RC-66047 is desired in the mill base, new levels (lower) of A-B dispersant will be required to minimize settling.

H-735	77.0		Instructions same as above except for stay time which should be 8-10 min.
448E-104	8.0		
W-819	15.0	(Monastral Red)	
	100.0		

Mill base formulations for other pigments mentioned in this report can be supplied on request.

APPENDIX, SECTION II

AUTOMOTIVE ACRYLIC ORGANOSOL PRODUCT - MILL BASE FORMULATIONS

Code	%		
H-47	15.0	Toluene	Add in order with mixing, mix 10 min.
H-79	15.0	Cellosolve Acetate	
H-13009	20.0	Silane dispersant	
W-839	20.0	Monastral Red	Add slowly with mixing, Mix 30 min.
Isopar "E"	20.0	Aliphatic solvent	

Add slowly with mixing, mix 10 min.

Grind "47P" 50/50 sand/base 20 min. staytime

H-47	10.0		Instructions same as above except first portion mix 1/2 hr. to insure solution of polymer
H-79	20.0		
9470-5	20.0	(Solution form organosol polymer)	
H-13009	20.0		
W-839	20.0		
Isopar "E"	10.0		

APPENDIX, SECTION II
(part two)

AUTOMOTIVE ACRYLIC ORGANOSOL - ORDER OF ADDITION

424E-163B

Code	%		
H-11947	66.25	Organosol Polymer	Add in order with mixing, mix 1/2 hr.
RL-G-32345	4.17	Plasticizer (I)	
RL-3340	4.51	Plasticizer (I)	
H-583	8.83	Xylene (I)	
424-E-151-C	1.66	W-839 Mill base (II)	Add in order with mixing, mix 1/2 hr.
424-E-134-B	2.65	Aluminum base (II)	
Isopar "E"	11.93	Non-solvent (III)	Add slowly with mixing, mix 1/4 hr.
	100.00		

Some modification to this formula may be required to insure optimum results with different formulations. It is expected that the ratio of H-583 to Isopar "E" will be the only variables to adjust.

424E-163B

Addition	Ingredient Code	%	#	Intermediate %	Intermediate #	% Solids	# Solids	Gal. Wt #/Gal.	Volume Solids	Volume Liquid	Pigment Volume	# Liquid
	Organosol Polymer							7.32 bulk				
1	H-11947	66.25	300.0	.4	120.0	40.0	120.0	9.61 solids	12.50	-	-	
	Isopar "E"			.34	102.0	0.0		5.98	-	17.10	-	102.0
	H-49			.8	24.0	0.0		7.18	-	3.3	-	24.0
	H-35			.18	54.0	0.0		6.66	-	8.1	-	54.0
2	RL-G-32345	4.17	18.9	.925	17.5	92.5	17.5	9.07 bulk 9.25 solids	1.9	-	-	
	Plasticizers			.075	1.4	0.0		7.78	-	.18	-	1.4
3	RL-3340	4.51	20.4	.853	17.5	85.3	17.5	9.28 bulk 9.78 solids	1.8	-	-	
				.147	2.5	0.0		6.25	-	.4	-	2.5
	Xylene											
4	H-583	8.83	40.0			0.0		7.16	-	5.6	-	40.0
	Millbase											
5	424E-151-C	1.66	7.5									
	Toluene H-47			.10	.75	0.0		7.18	-	.1	-	.75
	A-B Dispersant H-13009			.20	1.50	50.0	.75		0.5*	.10*	-	.75
	Cell. Acetate Solution Form			.20	1.50	0.0		8.06	-	.16	-	1.50
	Organosol			.20	1.50	25.00	.33	7.0 bulk* 9.6 solids*	.04*	.10*	-	1.10
	Pigment W-839			.20	1.50	100.00	1.5	12.60	.12	-	.12	
	Isopar "E"			.10	.75	0.0		5.98	-	.12	-	.75
	Aluminum Base											
6	424E-134-B	2.65	12.0									
	W-105			.2500	3.0	100.0	3.0	12.3	.24	-	.24	-
	H-11974			.6736	8.08	40.0	3.23	7.32 bulk 9.61 solids	.35	.75	-	4.85
	RL-3340			.0382	0.46	85.3	.40	9.28 9.78	.04	-	-	.06
	RL-G-32345			.0382	0.46	92.5	.43	9.07 9.25	.05	-	-	.03
7	Isopar "E"	11.93	54.0			0.0		5.98	-	9.0	-	54.0
		100.00	452.8				164.69		17.09	45.01	.34	287.69

62 10

Volume Solids = 27.5
Weight Solids = 36.5

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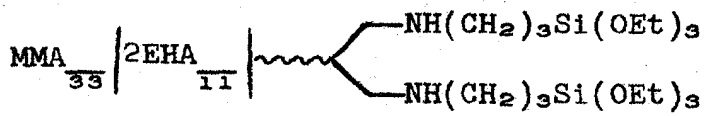
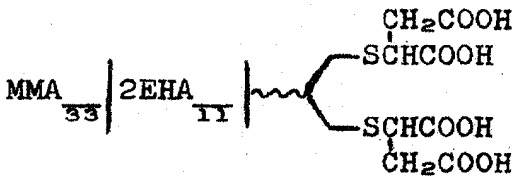
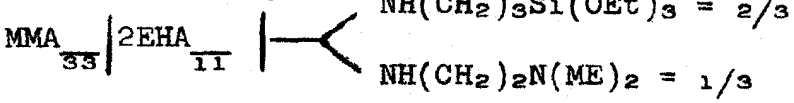
GLOSSARY

Silane dispersant 

Acid function dispersant 

Mixed Silane-Amine functionality 

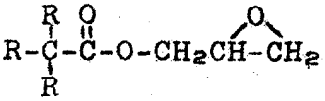
MMA = Methyl Methacrylate

2EHA = 2 Ethyl Hexyl Methacrylate

HEH = Hydroxy Ethyl Methacrylate

Phthal. Anh. = Phthalic Anhydride

Cordura E = Glycidyl ester of versatic acid



Desmodur "N" = Trifunctional isocyanate

W-74 = TiO_2

W-362 = Iron oxide (coarse pigment)

W-608 = Nickle - TiO_2 complex - yellow pigment

W-686 = Pb-Chromate yellow pigment

W-577 = Phthalo cyanine blue pigment

W-819 = Quinacradone Red pigment

W-839 = Quinacradone Red pigment

ABSTRACT

The ability of A-B dispersants to deflocculate pigment dispersions is established. The effect of A-B dispersants on film and product properties will be determined. Dispersions containing A-B type dispersants were supplied to the Marshall Laboratory for evaluation of film and product properties in the L.B.A. urethane enamel product system. Formulation of dispersions using A-B dispersants for use in the acrylic organosol product continues. Initial results are good and work indicates the possibility of stable high solids product system.

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