E. I. DU PONT DE NEMOURS & CO.
FABRICS AND FINISHES DEPARTMENT

GARFIELD LABORATORY
EXPLORATORY RESEARCH REPORT

SUBJECT: PREVENTION OF FLOCCULATION OF MONASTRAL BLUE PIGMENTS

DATE ISSUED: OCTOBER 16, 1945

PERIOD COVERED: 11/9/45 - 7/30/46

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Study: Prevention of Flocculation of Monastral Blue Pigments

I. Introduction

Lacquer compositions which include Monastral Blue pigments show marked signs of flocculation after standing for several hours. Further storage results in complete flocculation and separation into two or more layers. Monastral Blue flocks and the other pigment or pigments involved. This is particularly evident when Monastral Blue is mixed with white to produce lighter shades of blue.

When Monastral Blue was first introduced as an active lacquers several years ago, complaints of "rapid settling" were received. However, since the automotive industry is equipped to agitate and circulate the lacquers continuously, no serious problem is encountered. On the other hand, in the varnish and industrial trade, complaints were so numerous that the use of Monastral Blue pigments was not only retarded, but, in a large number of varnish products, it was necessary to eliminate Monastral Blue entirely. Therefore, the problem under consideration is to produce a Monastral Blue lacquer which will not flocculate or separate in the interim between packaging and use.

II. SUMMARY AND CONCLUSIONS

Early in 1934, a limited amount of work was conducted at the Perth Laboratory towards the prevention of flocculation of Monastral Blue in lacquers by the addition of small amounts of either surface active agents or materials which might be considered dispersion agents.

Further work recently completed involving the evaluation of a number of additional agents has resulted in the selection of C-1014, a Hercules ethyl cellulose of low ethoxyl content (43.5%), as a treating agent which will successfully prevent the flocculation of Monastral Blue pigments.

The most attractive method of treatment is the addition of a 10% ethyl cellulose solution to the finished product lacquer accompanied by a short period of stirring. The amount of agent necessary is 0.5% granular ethyl cellulose computed on a total weight of batch basis.

Laboratory samples so treated have now been standing for five months with no signs of flocculation evident.

III. Experimental

A. Determination of Promising Agents

The problem of flocculation prevention has been given considerable attention not only by the F. & F. Department, but Organic and Pigments Departments as well.

At the start of the present work, it was decided that the best method of attack was to use small amounts of either surface active agents or materials which might be considered as dispersion agents. These agents or materials could be added to the existing standard formulas at different stages, wherever convenient.

The standard or basis formulas referred to are listed below:

1. Blue Pulp Process: This is a modified version of the standard pulp process developed for Monastral Blue pulp.

M. A.P. Grind

VX-7800 (dry)	46.7%	
Monastral Blue Pulp (dry)	17.8	Mix thoroughly
Dispersion Agent*	10.0	
X-140		Mix 10 minutes
X-117		
X-214	17.2	Grind colloid 20 mins.
Monastral Blue Pulp (dry)	4.2	Mix 10 minutes
X-111	4.0	Grind colloid 20 mins.
	100.0%	Sheet and Dry

*For the treated experiments, the agent is added at this point. The percentage depends upon the individual run and the difference is proportionally taken from each of the other ingredients.

Finished Lacquer Make-up

Pulp Process Stock	16.4%	Mix until stock is
X-29	10.0	completely in solu-
X-6	13.1	tion and no gels is
X-35	10.0	observed on a glass
X-12	3.2	plate smear.
X-161	27.9	
X-111	2.7	
X-120	2.4	Mix until homogene-
X-51	7.9	ous
XL-272	7.6	
X-29	1.5	
	100.0%	

White Backing Sheet Make-up (253-2953)

First Portion	
B-369	47.6%
B-361	1.0 Mix 1 hour
PX-1026	14.9
Second Portion	
K-115	1.8
K-117	2.4 Mix 1/2 hour
K-12	1.0
B-6	6.4
Third Portion	
0-678	0.3
2L-272	23.6 Mix 1 hour
	100.0%

5. Combination of Blue and White Pulp Process

M. & P. Grade

PX-7600 (dry)	48.90%
Agent	2.45 Mix thoroughly
Manastral Blue Pulp (dry)	1.45
K-26	23.60
K-120	7.00
K-111	16.60
	100.00% Sheet and Dry

Finished Lacquer Make-up

K-6	25.4%
K-29	7.2
K-35	7.2
K-1	7.2
K-12	7.2
B-363	8.2
Above Stock	29.2
K-111	0.5
K-120	1.2
KL-272	7.6
	100.0%

6. Each of the above formulas, other than No. 5, when made up must then be mixed with the opposite color (blue with white or white with blue) to determine the flocculation or dispersion characteristics of the system. The Standard Flocculation Test Formula is as follows:

Blue Lacquer	20%
White Lacquer	80
	100%

The initial work of the problem was concerned with obtaining and testing a number of materials in one or more of the aforementioned formulas. The following is a list of these materials:

Dynamite Nitrocellulose
Polyvinyl Acetate
Nasoin
Carboxymethocel (Sodium Salt)
Polyvinyl Alcohol
Cellulose Acetobutyrate
Cellulose Acetate
Ethyl Methacrylate
Polyvinyl Butyral
Vistanex
Kadox
Barium Hydroxide
Phosphoric Acid
Aerosol
Soya Bean Lacquer Oil
Tween 85
Armeryx T
G 825 (Atlas-ol 1)
Lecol
Diglyco Stearate
Phil a sol
Aske 450
Tween 81
Tritheil Base 265
Span 60
Span 80
Tween 20
Methyl Cellulose
Ethyl Cellulose

Of the above list, three agents showed considerable promise. They are ethyl cellulose, methyl cellulose, and dynamite nitrocellulose. However, upon broadening the investigation of each, all but one - ethyl cellulose, were eliminated as being impractical for plant use because of their narrow workable range.

B. Determination of Optimum Amount of Ethyl Cellulose

Two factors were involved in the establishment of the optimum amount of ethyl cellulose. First, the smallest workable amount of ethyl cellulose had to be found; and next, a sufficient safety factor had to be incorporated into this value to make it feasible for plant operations.

A series of experiments containing decreasing amounts of ethyl cellulose was run until the lower limit was determined. This limit was then used as a basis for further experimentation resulting in the adoption of 0.5% granular ethyl cellulose (computed on the total weight of batch) as the optimum amount of ethyl cellulose necessary to prevent the flocculation of Monastral Blue pigments in the "standard" formulas.

C. Methods of Addition of Ethyl Cellulose

The initial runs with ethyl cellulose all employed the use of ethyl cellulose in its granular form. However, glass smear tests of many of these runs indicated that not all of the ethyl cellulose granules had dissolved and the small "fines" that were left produced a grainy

*See "standard" formulas on page 2.

finished product. Therefore, it was decided to test the effectiveness of ethyl cellulose when added as a solution or base.

Numerous solvents and solvent combinations for ethyl cellulose, as well as varying strengths of solutions were tried with the following adopted as the standard ethyl cellulose treating solution:

Standard 10% Ethyl Cellulose Treating Solution

		100 g. Basis
Toluol (H 27)	80%	72 g.
Denatured Alcohol (S-1)	20	18
	100%	90 g.
S-1014		10
		100 g.

*S-1014 is the code given to a certain brand of ethyl cellulose. For details see page 7.

This 10% ethyl cellulose treating solution was then tested in all of the standard formulas listed under III-A page 2 and was found to be satisfactory not only from the flocculation standpoint, but also as far as the small "rings" and grit were concerned. In the testing of the standard formulas, tests were also made on varying percentages of blues from 0% to 100%. The results of this work indicate that a non-flocculated system results when:

1. A treated blue lacquer is admixed with an untreated white lacquer
2. A treated white lacquer is admixed with an untreated blue lacquer
3. A treated blue and a treated white lacquer are admixed.

Along with these tests it was discovered that the treating solution need not be added during the make up of the different standard formulas as was heretofore done, but could be added at the very end of the make-up as a "stabilizer" with only a short period of stirring necessary. This, being a far superior method of addition, is the present adopted procedure.

D. Determination of Best type of Ethyl Cellulose

In the early "scouring" work of the problem, ethyl cellulose was tested along with a number of other possible agents. The ethyl cellulose used was a specially-ordered type being used in connection with another problem.

With the completion of sufficient experimental data to demonstrate the possibilities of ethyl cellulose, it was then deemed advisable to concentrate further upon this individual agent.

Since the plant did not stock this "special" ethyl cellulose, but did stock four other types, a series of evaluation runs were conducted. The results of these runs are tabulated below:

Type		Results	Remarks
A.	G-1014 Plant-stocked	Very Good	This is the type adopted for use.
B.	G-1017 " "	N.G.	Viscosity too high for practical use.
C.	G-1022 " "	N.G.	Viscosity too low. Also flocculation not prevented.
D.	G-1025 " "	Very Good	Very similar to G-1014. Possible that substitution can be made.
E.	G-1039 "Special"	Very Good	All results have been satisfactory.

Although the G-1014 and the G-1025 were very similar, the G-1014 produced a slightly superior base or solution and, therefore, was adopted as the treating agent.

E. Miscellaneous

1. Durability Room Tests - The durability of both "treated" and "untreated" metallic lacquers is being checked at this present time. Six different formulas are currently being stored in the "treated" and "untreated" state.

[illegible] ethyl cellulose lacquer [illegible] color [illegible] slight improvement in durability [illegible] ethyl cellulose tends to increase the flexibility [illegible] Also, ethyl cellulose lacquers retain their color [illegible] greatly well as [illegible] to sunlight. This might afford a reduction in the housing effort of Monsanto Plastics Plant.

2. Monsanto Green Pigmented - In connection with the [illegible] Lab ought discovered, it was found that the [illegible] solution is also a [illegible] Monsanto Green pigmented [illegible] [illegible] [illegible] [illegible]

DETAILED TABLES OF ETHYL CELLULOSE EXPERIMENTS

TABLE I — ETHYL CELLULOSE TREATMENT OF THE WHITE PIGMENT

A — REGULAR ETHYL CELLULOSE:

Notebook Exp. No.	Description and Conditions	% Agent	Process	Observations
WP 1A	Ethyl cellulose treated TiO_2	10% on TiO_2	White Pulp Process	No flocculation observed
WP 23A	Ethyl cellulose treated TiO_2	2.5% on TiO_2	" " "	" " "
WP 23B	Duplicate of WP-1A	7.5% on TiO_2	" " "	" " "
		5.0% on TiO_2	" " "	" " "
		0.5% on TiO_2	" " "	Flocculation in 24 hrs.
WP-24A	Series of blends of 10% treated white and untreated blue: 10% blue - 90% white 20% blue - 80% white 35% blue - 65% white 50% blue - 50% white 75% blue - 25% white	10% on TiO_2	White Pulp Process	No flocculation observed Flocculation in 7 days Flocculation in 22 days Some flocculation in 1 month No flocculation observed
WP-45	Mixing 253 line tinting enamels with 10% ethyl cellulose treated 253-0953	See results of WP-79, 80, 81		
WP-69B	Series of blends of ethyl cellulose treated white and untreated blue: Samples of 50% blue and 25% blue Samples of 20% blue and 35% blue Sample of 10% blue	10% on TiO_2	White Pulp Process	Flocculation in 25 days Semi-flocculation in 1 week No flocculation observed

	Description and Remarks	% Agent	Process	Observations
[illegible]	Series of ethyl cellulose solutions treated white and factory blue	10% on TiO_2	White Pulp Process	No flocculation noticed on series from 10% blue to 75% blue
[illegible]	Series of ethyl cellulose solutions treated white and factory blue	8% on TiO_2	White pigmented base Process	No flocculation observed in series
[illegible]	ETHYL CELLULOSE TREATMENT OF BLUE PIGMENT			
[illegible]	A - CHEMICAL ETHYL CELLULOSE			
[illegible]	Ethyl cellulose treated blue	20% on blue	Blue Pulp Process	Flocculation in 24 hrs.
[illegible]	Ethyl cellulose treated blue	32% on blue	" " "	No flocculation observed in
[illegible]	Ethyl cellulose treated blue	23% on blue	Blue Ball Mill Process(253-059)	Flocculation in 3 days
[illegible]	Ethyl cellulose treated blue using plant-stocks ethyl cellulose (0-10%)	30% on blue	Blue Pulp Process	No flocculation observed
[illegible]	B - ETHYL CELLULOSE SOLUTION			
[illegible]	Series of ethyl cellulose solutions treated mill base blue and factory white	30% on blue	Blue Ball Mill Process	No flocculation noticed in series
[illegible]	Series of ethyl cellulose solutions treated mill base blue and factory white	10% on blue	Blue Pulp Process	No flocculation observed in series

...OF DUPONT WHITE AND IRON PIGMENTS

...Ethyl Cellulose

Notebook Exp. No.	Preparation and Conditions	% Agent	Process	Observations
WF-39	Ethyl cellulose solution added to a mixture of two finished lacquers - Control			
	Ethyl Cel. treated white (WF-38A)	10% on white	-	No flocculation observed
	Ethyl Cel. treated blue (WF-32)	23% on blue	-	
WF-41	Ethyl cellulose solution added to a mixture of two finished lacquers - Control			
	Ethyl Cel. treated white (WF-38A)	5% on white (outbook)	-	No flocculation observed
	Ethyl Cel. treated blue (WF-32)	23% on blue	-	
WF-43	Ethyl cellulose added to a mixture of two finished lacquers	0.5% on total wt. of mixture	Factory materials used	No flocculation observed
WF-44	Ethyl cellulose solution added to a mixture of two finished lacquers - Control			
	Ethyl Cel. treated white (WF-38A)	(See WF-23A and WF-32)		No flocculation observed
	Ethyl Cel. treated blue (WF-32)			
WF-47	Ethyl cellulose solution added to a mixture of two finished lacquers - Control	0.56% on total wt. of mixture	Two factory materials	No flocculation observed
WF-48	Mixtures of varying percentages of blue and white with approximate amount of ethyl cellulose needed	0.56% on total wt. of mixture	Factory materials	0%, 10%, 20%, 100% blank no flocculation observed 30%, 40%, 50%, 60%, 70%, 80%, 90% blue - seed flocculation occurring

...ETHYL CELLULOSE SOLUTION

WF-49	Ethyl cellulose solution added to a mixture of two finished lacquers	0.56% on total wt.	Factory materials used	No flocculation observed
WF-50	Mixtures of varying percentages of blue and white with approximate amount of ethyl cellulose needed	0.56% on total wt.	Factory materials used	Flocculation or seeding times noted in all samples

[illegible] ON BOTH WHITE AND BLUE PIGMENTS (continued)

[illegible]

[illegible]	[illegible] and [illegible]	% Agent	Process	Observations
[illegible]	[illegible] 10% [illegible] "[illegible]" [illegible] (55% blue)	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	Same as FT 611, [illegible] 10% [illegible]	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	Same as FT 611, [illegible] 50% [illegible]	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	Same as FT 611, [illegible] 70% [illegible]	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	Same as FT 611, [illegible] 30% [illegible]	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	Same as FT 611, [illegible] 5% blue	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	Same as FT 611, [illegible] 95% [illegible]	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	[illegible] of D-1022 [illegible]	0.56% total wt.	Factory materials	Flocculation in [illegible] hrs.
[illegible]	[illegible] effectiveness of # 1025 [illegible]	0.56% total wt.	Factory materials	No flocculation observed
[illegible]	[illegible]			
[illegible]	[illegible] 25% [illegible] [illegible]	0.56% total wt.	Lab. made vehicles	Treating solution [illegible] pattern
[illegible]	[illegible]	(see adopted solution on p. 6)		

TABLE [illegible] - MISCELLANEOUS (continued)

[illegible] No.	Description and Conditions	% Agent	Process	Observations
WP 66	Viscosity of ethyl cellulose as a function of agent effectiveness	0.56% total wt.	Factory materials	Viscosity in question has no effect on flocculation
WP 68	Effect of a 101% solution on a mixture of 253 0953 and other 253 line tinting enamels	(see results of WP-79, 80, 81)		
WP 79	Untreated 253 0953 combined with all available 253 line tinting enamels (standard for WP 80 and WP 81)		Factory materials	Monastral Blue and Green samples in dicate no floccu- lation. All other samples remain un- changed from the WP 79 untreated standards
WP 80	Treated 253 0953 combined with treated 253 line tint- ing enamels	0.5% total wt.	Tumbled tinting enamels mech. stirred 253 0953	
WP 81	Treated 253 0953 combined with untreated 253 line tinting enamels	0.5% total wt.	Mechanically stirred 253 0953	

CODE APPENDIX

E-1	Denatured Alcohol
E-6	Butyl Acetate
E-12	Butyl Alcohol
E-15	Xylene
E-29	Petroleum Naphtha
E-30	Acetone C.P.
E-35	Methyl Ethyl Ketone
E-47	Toluene C.P.
E-51	Hi-Solvency Petroleum Naphtha
E-111	Dibutyl Phthalate
E-112	Blown Castor Oil
E-120	Pale Blown Castor Oil
E-136	Ethyl Acetate
E-205	Butyl Cellosolve
E-165	PK Base
E-501	PK Base
E-578	PK Base
E-26	Titanium Oxide L.O.
E-505	Monastral Fast Blue
G-672	Malic Acid
G-1014	Ethyl Cellulose P-50
G-1017	Ethyl Cellulose P-200
G-1022	Ethyl Cellulose K-14
G-1025	Ethyl Cellulose E-100
G-1059	Ethyl Cellulose - Special Lab. Ordered
EL-7809	1/4 Sec. Nitrocellulose - Water Wet
EL-272	Hydrogenated Castor Oil (Modified Resin)

(Resin Code No. EL-267)

AGENT APPENDIX

Aero 450	Sodium petroleum sulfonate - Stanco Inc.
Aerosol (O.T.)	Alkyl sulfonate - Dioctyl ester of sodium sulfosuccinic acid - American Cyanamid and Chemical Corporation
Ammonyx T	Quaternary Ammonium Salt Trialkylbenzyl-ammonium chloride - Onyx Oil and Chemical Company
Daxad	Aromatic Sulfonate - Polymerized sodium salts of alkyl naphthalene sulfonic acids - Dewey & Almy Chemical Company
G-666	Alkanol B
Phi o sol	Alkyl Sulfate - Sodium salt of sulfonated ricinoleic acid ester - Onyx Oil and Chemical Company
Span 40	Fatty Ester - Sorbitan Monopalmitate - Atlas Powder Company
Span 60	Fatty Ester - Sorbitan Monopalmitate - Atlas Powder Company
Tween 20	Polyether - Polyoxyalkene ether of partial lauric acid ester - Atlas Powder Company
Tween 61	Polyether (same as Tween 20 substituting stearic acid)
Tween 65	Polyether (same as Tween 20 substituting oleic acid)
Triton B-1956	Tween 80 Polymers - Sodium Sulfonates of Mineral Oil - Rohm & Haas Industries, Inc.

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3. Surface-Active Agents - G. B. F. Young and K. W. Goons; Chemical Publishing Co., Inc.; Brooklyn, N. Y.

4. Standard Practice and Data Book - Parlin Laboratory

5. Ethyl Cellulose - booklet; Hercules Powder Company

6. Prevention of Flocculation of Monastral Blue - Letter R. F. Hucks to P. B. Cochran; May 29, 1945

Note: All work described in this report (unless otherwise noted) is covered in Notebook 2153 issued to William F. Schneller November 9, 1945.