9-6 HUMIDITY RESISTANCE - "MONASTRAL" MAROON By: H. Matrick 6/68 - 8/68

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

HUMIDITY RESISTANCE - "MONASTRAL" MAROON

Period Covered June - August, 1968 (Part time)

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NEWARK PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: HUMIDITY RESISTANCE - "MONASTRAL" MAROON

PERIOD COVERED: June - August, 1968 (Part Time)

SUBMITTED BY: H. MATRICK Date Submitted: 2/18/69

APPROVED BY: F. F. EHRICH Date Released: 3/3/69

ABSTRACT

Iron pyrophosphate (10%) and aluminum benzoate (50%) were the only extenders which improved the humidity resistance of "Monastral" Maroon, RT-792-D, in acrylic lacquer films over an unextended, well-washed toner. Commonly used extenders such as nickel carbonate and calcium Staybelite showed deleterious effects. Water soluble impurities likewise showed deleterious effects. Degree of dispersion was not an important factor.

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I. INTRODUCTION AND OBJECTIVES

In May, 1968, F. and F.,Flint, reported (see Appendix A) that RT-792-D, "Monastral" Maroon, had failed General Motors' humidity test. This put the use of RT-792-D and other quinacridones in 1969 automotive finishes in jeopardy of being discontinued. The object of this investigation was to determine the causes of poor humidity resistance of RT-792-D. The factors under suspicion were impurities, pigment extenders, and degree of dispersion.

II. SUMMARY AND CONCLUSIONS

Iron pyrophosphate (10%) and aluminum benzoate (50%) have been found to have a beneficial effect upon the humidity resistance of RT-792-D. This information has been transmitted to F. and F., Flint.

All other commonly-used extenders have varying deleterious effects upon humidity resistance, the worst being calcium Staybelite. Likewise, nickel carbonate, alumina hydrate, and blanc fixe appear to be harmful. Water-soluble impurities have a deleterious effect. Alcohol-soluble impurities (Emcol P-1059) do not effect humidity resistance.

Degree of dispersion is a minor factor or not important at all in humidity resistance performance.

III. PATENT STATUS

A patent proposal (CP-98) has been submitted on humidity resistance improvement of acrylic lacquer films by iron polyphosphates (See Appendix B, p. 6).

IV. DISCUSSION

In this study, pigments were evaluated as to their contribution to humidity resistance of a lacquer film by first 2-roll milling with cellulose acetate butyrate resin. The chips were reduced in an acrylic lacquer formula containing the plasticizer benzyl butyl phthalate and solvents. Masstone panels were prepared by drawdown. The panels were baked, then exposed to 150°F. and 100% humidity for 16 hours.

It was found (B.J.Godfrey) that humidity resistance behavior is dependent on the bake temperature. This can be explained in terms of the degree of plasticity of the film. K. Batzar* has shown that water is transported through the film by osmotic pressure effects. This transport is related to the plasticity or specifically the glass-transition temperature. When this temperature is below the humidity test temperature, 150°F. water transport occurs readily. The glass-transition temperature increases with decreasing plasticizer content. During the baking cycle, the partially volatile plasticizer benzyl butyl phthalate is partially lost, thus effecting humidity resistance.

*KN-68-3

Two bake ovens have been used which deliver films of different plasticities, a 275°F. temperature bake on one oven liberates a considerable amount of plasticizer and a "285°F." bake which in effect spends little time at 285°F. and, therefore, liberates less plasticizer. The latter cycle gives a film which is more sensitive to humidity and to factors which effect humidity resistance.

A. Effect of Impurities

The RT-792-D rejection by F. and F. was complicated by a change in plant formula made in 1966 which eliminated the final washing of this product. A temporary standard or so-called shipping lot was based on this procedure. Table I shows the result of humidity resistance tests vs. other plant materials which were washed.

TABLE I

HUMIDITY RESISTANCE OF PLANT LOTS OF RT-792-D

Lot	Wash	Status	275°F	"285°F" Bake	% Water Soluble Matter	Electrical Resistiv't. Ω
SL89679	No final	Tem.Std.	poor	poor	1.1	1,500
PS97569	Final	Prev."	good	poor	0.65	4,800
90558	Final	Prop."	good	poor	0.48	4,000
54749	Final	Pres. plant prod.	good	-	0.45	10,500

It is apparent that to maintain good humidity resistance at 275°F. bake, RT-792-D requires press washing as opposed to center-feed pressing which precludes washing. Normal plant product washed to 4000 Ω appears to give reasonably acceptable performance at 275°F. bake. Extracts of the unwashed SL-89679 showed presence of Na^+, Cl^-, and Ca^{++} which would be expected from the final calcium Staybelite laking. Further clarification of the effect of water and alcohol-soluble impurities was obtained by further washing a "Monastral" Maroon presscake, RT-801-P, which had been plant washed to 4800 Ω, to 20,000 Ω in the laboratory using distilled water. A third sample was prepared by washing the 20,000 Ω presscake with alcohol 2B followed by washing with distilled water to remove the alcohol. The presscake was dried directly and not extended before evaluation. Humidity resistance results are summarized in Table II. A rating system was used in which a 10 rating represents no change and a 0 rating represents total film destruction in which gloss is completely destroyed as is color strength.

TABLE II

EFFECT OF IMPURITIES ON HUMIDITY RESISTANCE OF UNEXTENDED "MONASTRAL" MAROON

Sample	Final Wash Resistivity	Humidity Resistance 275°F.	"285°F"
Plant washed	4,800	9	7
Lab H_2O washed	20,000	10	8
Lab alcohol washed	60,000	10	8

Thus, it appears that at a 4,800 ohm wash, sufficient water-soluble impurities are present to cause some downgrading of humidity resistance. Removal of alcohol-soluble impurities such as the anionic surfactant Emcol P-1059 does not further improve humidity resistance.

B. Effect of Extenders

The previously discussed 20,000 ohm sample was treated with various extenders most by co-pulverization but, in some cases, by in situ precipitation. In these cases, the samples were washed to 8,000 ohms. Results are summarized in Table III.

TABLE III

EFFECT OF EXTENDERS ON THE HUMIDITY RESISTANCE OF "MONASTRAL" MAROON

Extender	%	Method of Combination	Humidity Resistance 275°F.	"285°F"
None			10	8
calcium Staybelite	10	Precipitated	9	0
" "	10	Co-pulverized	9	0
Nickel carbonate	10	Precipitated	8	6
" "	10	Co-pulverized	7	0.5
Barium sulfate	10	"	9.5	6
Alumina hydrate	10	"	10	3
Aluminum benzoate	50	Precipitated	10	9
Iron pyrophosphate	10	Co-pulverized	9.5	10

Note that all extenders except iron pyrophosphate and aluminum benzoate downgrade humidity resistance. An interesting fact is that calcium Staybelite performs well at 275°F. but leads to total film destruction at"285°F.". Thus, calcium Staybelite is a highly undesirable extender for pigments in automotive finishes. It is also significant that precipitated nickel carbonate, although not totally satisfactory, performs better than dry-pulverized nickel carbonate. This suggests that commercial nickel carbonate contains deleterious water-soluble impurities.

To further exploit the iron pyrophosphate lead, the latter was dispersed separately in CAB, then reduced and added to "Monastral" Maroon dispersions. These results are summarized in Table IV.

TABLE IV

EFFECT OF 10% IRON PYROPHOSPHATE ON HUMIDITY RESISTANCE OF VARIOUS "MONASTRAL" MAROON SAMPLES

Sample	Humidity Resistance 275°F.	"285°F.
20,000 washed no extender	9.5	7.0
" " " " + $Fe_4(P_2O_7)_3$	9.0	9.5
SL-86979, unwashed RT-792-D	0	0
" " " + $Fe_4(P_2O_7)_3$	3	1.5
55865, 5000 RT-792-D, no CaSx	9.5	6.0
" " " + $Fe_4(P_2O_7)_3$	9.5	9.0

It has also been demonstrated that $Fe_4(P_2O_7)_3$ improves the humidity resistance of clear films. Thus, iron pyrophosphate appears to improve humidity.resistance regardless of the purity of the RT-792-D used. Nothing is known about the mechanism by which iron pyrophosphate operates. It is possible that it somehow lowers film plasticity.

C. Degree of Dispersion

Several experiments were run to try to determine if degree of dispersion had an effect on humidity resistance. In all cases, results showed degree of dispersion was not important. In one experiment, a sample was chipped with internally and externally added QAAF. In another, ball-milled, sand-milled, and CAB-chipped "Monastral" Maroon were compared. In a third experiment, sand milling was carried out for varying lengths of time. In all cases, 20,000 ohm"Monastral" Maroon without extender was used. Again, no major differences in humidity resistance could be detected as a result of varying dispersion.

dc

JHM
DFFE

FFE-EED

J.H.Baird, Pigm. Wilm.
J.E.Kramer, Pigm. Wilm.
S.J.Gorman/L.F.Andrews, Pigm.Wilm.
P.D.Graham, Pigm. Wilm.
R.H.Zabel, Pigm. Wilm.
M.Hunt/T.Gerick, Pigm. Wilm.
Pigments Wilmington File

W.F.Spengeman/H.B.Clark, C.R.
~~A.T.Lewis~~, C.R.
~~H.S.Struve~~/A.A.Brizzolara, Pigm. Newark
~~R.H.Wetzel~~, Pigm. Newark
Pigments Chestnut Run File

OFFICE TRADE REPORT

F&F - FLINT

REPORTED BY: J. A. Lamiet

DATE OF CALL: 5/9/68

Wes Bullock telephoned to report a number of quinacridone pigments failed the General Motors' humidity test (my office trade report, 5/7/68). These pigments are in order of increasing stability to the humidity test: Monastral® Maroon RT-792-D; Monastral® Violet R, RT-733-D; Monastral® Violet R, RT-819-D; and Quindo Violet RV-6902-D. RT-819-D and RV-6902-D are about equal and are considered possibly borderline in acceptability. Thiofast Red Toner MV-6606 and Thiofast Red Lake MV-6655 apparently pass this test. The test is now reported to be run for only 16 hours, rather than the 24 hours previously reported. The temperature of 150°F. and 100% relative humidity conditions remain unchanged. Bullock indicates that the '69 maroon basically formulated with RT-792-D and the solid red formulated with RT-733-D, molybdate orange, and iron oxide fail this test. Accordingly, the consumption of quinacridones for General Motors' automotive finishes for the 1969 model year is currently in jeopardy unless an answer is found quickly. Chestnut Run has just placed an order for equipment to run this test; meanwhile, Flint has offered us their facilities for any tests that we may wish to run to help resolve this problem.

/akr

CC: W.S.Struve/A.A.Brizzolara
F.F.Ehrich
R.D.Nutting, Newport
M.Hunt/E.Gonick, Pigts.,Wilm.

Newark, New Jersey
February 4, 1969

MISS JANE E. MACRUM
Pigments - Newport

PATENT PROPOSAL CP-98

HUMIDITY RESISTANCE IMPROVEMENT OF ACRYLIC LACQUER FILMS BY IRON POLYPHOSPHATES (PYROPHOSPHATES)

This invention involves compositions of matter consisting of a mixture of an acrylic thermoplastic lacquer film with a ferric polyphosphate (pyrophosphate). Such compositions render the paint film resistant to decomposition by water or water vapor, a property which is particularly crucial to acceptable performance of automotive finishes.

A typical thermoplastic acrylic lacquer film consists of polymethyl methacrylate resin, cellulose acetate butyrate resin, and a plasticizer. When such film, with or without pigment, is subjected to heat and water vapor or condensing water, considerable deterioration occurs. The problem is evident on automotive lacquer and is particularly severe in warm, humid areas of the U. S. Such conditions can be simulated and accelerated by various testing devices, the most commonly type used being the Cleveland Humidity Cabinet. Here paint films on metal panels are exposed to 100% relative humidity at elevated temperatures (80-180°F.). An acrylic lacquer film,when exposed to these conditions for a few hours, will develop a non-uniform hazy, cloudy appearance with accompanying loss of gloss, so-called "water spotting". As degradation proceeds, the film will become opaque and lose all reflective ability. A transparent film pigmented with a colored toner will become opaque with accompanying lightening or loss of coloring strength. Use of iron polyphosphate simply added to the wet acrylic lacquer produces a film with much superior resistance to humidity degradation. Often these films show no visible indication of degradation even after 16 hours of exposure in a humidity cabinet at 150°F.

Another advantage of this invention relates to the use of iron polyphosphate as an extender for colored pigments used in acrylic lacquer systems. Colored toners are commonly produced with 10% of a colorless transparent material, often an inorganic salt. One important function that these extenders perform is to allow standardization of tinting strength of the product. Often, they will serve another function such as improving dispersibility or lightfastness. It has been found these extenders have a deleterious effect on humidity resistance. Among them are blanc fixe, alumina hydrate, basic nickel carbonate, and calcium rosinate. Iron polyphosphate is unique in that it is the only otherwise suitable extender tested that does not have a deleterious effect, let alone a beneficial effect, on humidity resistance.

To date, we have worked with 10% iron pyrophosphate, A-33-D, and 90% "Monastral" Maroon toner. This composite pigment was prepared by drying RT-801-P and co-pulverizing the two materials. CAB dispersion was prepared in the usual manner (described in Example VII, CP-87). The dry paint film composition consisted of 7.5% composite pigment or 0.75% iron pyrophosphate.

The following data were obtained by exposing "Monastral" Maroon with 10% of various extenders in the Cleveland humidity cabinet for 16 hours at 150°F. Two different type bake cycles were used. One type spends most of the time at 275°F. A second type "tops out" late in the cycle at 285°F., but the average temperature is effectively less than 265°F. The latter cycle gives paint films which are more sensitive to humidity. An arbitrary rating system was used with 10 designating no change and 0 designating maximum change.

Re: N.B. 1888-30, pp. 64,65,80,81

	275°F. Bake	"285°F." Bake
No extender	10	8
Ca Rosinate, dry blend	9.0	0.0
Blanc fixe, " "	9.5	6
Alumina hydrate, dry blend	10	3
Basic Ni carbonate, dry blend	7	0.5
A-33-D	9.5	10

Other workers have confirmed these results since this experiment was performed. R. F. White mentions in his Nov. 28 - Dec. 31, 1968 Monthly Summary that A-33-D is the only extender tested which did not adversely effect humidity resistance of "Monastral" Maroon. Likewise, C. W Manger mentioned in his Nov. 19 - Dec. 19, 1968 Monthly Summary that "Monastral" Maroon with A-33-D gives better results vs. a toner control.

PRIOR ART

U.S. 3,074,895, J. Jackson, 1963, claims coating compositions comprising 10-20% iron polyphosphate with either an alkyd vehicle (enamel) or oleoresinous varnish. Examples include both alkyd enamel and nitrocellulose lacquer.

MODIFICATIONS AND EQUIVALENTS

C. W. Manger's work indicates improvements can be made on an unpigmented lacquer. The invention should be tested with several pigments. Composition limits and composition of maximum effectiveness have yet to be determined. J. Jackson is doing some work on variation of the polyphosphate anion composition in addition to varying the cation. Jackson's 3,074,895 disclosed use of both pyrophosphate and tripolyphosphate. Also disclosed are use of compositions containing both sodium and potassium. C. W. Manger has shown A-33-D to be more effective when washed more extensively.

Variations in the lacquer formula might be considered such as omitting CAB resin or varying the plasticizer composition. Coverage might be extended to thermosetting acrylic enamels.

Combining the polyphosphate and pigment could be tried in several different ways: (1) precipitating iron polyphosphate in the presence of pigment slurry; (2) co-pulverizing the two materials; (3) formulating the additive directly into the paint system with the pigment; and (4) dispersing pigment and A-33-D separately and combining mill bases.

The acrylic lacquer dispersion can be prepared either by CAB dispersion, sand milling, or ball milling.

INVENTION RECORD

The first experiment concerning use of A-33-D for humidity resistance was begun by H. Matrick on May 14, 1968. The use of this material as a solution to the humidity resistance problem was conceived within about a week of this date by H. Matrick. On May 21, 1968, a work request was written for evaluation of samples in paint. Paint panels were prepared on June 14, 1968. The following statement is taken verbatim from F. F. Ehrich's (H.M.) Monthly Summary of July 17, 1968, and represents the first written disclosure of results of evaluation:

> "Iron pyrophosphate, A-33-D, has been shown to improve humidity resistance on a variety of "Monastral" Maroon samples. The A-33-D was chipped separately, reduced to a mill base and the latter added in a 10% amount to RT-792-D mill bases. In all

cases where improvement was possible, an improvement was shown. This included low bake and 275°F. bake films and samples with and without CaSx, and with varying degrees of soluble salts including the high solubles RT-792-D, SL 86979. This finding has been transmitted to F and F, Flint. Other systems such as clear films RT-819-D, "Monastral" Violet, "Afflair", and "Krolor" are being treated with A-33-D to determine its effect on humidity resistance. Evaluation in TAE-3 with RT-792-D and A-33-D is also underway."

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