KN-69-9 STUDIES ON THE IMPROVEMENT IN HUMIDITY RESISTANCE OF INORGANIC AND ORGANIC PIGMENTS IN "927" ACRYLIC LACQUER
By: J. Jackson 11/68 - 7/15/69

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STUDIES ON THE IMPROVEMENT IN HUMIDITY RESISTANCE OF INORGANIC AND ORGANIC PIGMENTS IN "927" ACRYLIC LACQUER

Period Covered November, 1968 - July 15, 1969 (Part time)

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

SUBJECT: Studies on the Improvement in Humidity Resistance of Inorganic and Organic Pigments in "927" Acrylic Lacquer

PERIOD COVERED: November, 1968 - July 15, 1969 (Part time)

SUBMITTED BY: J. Jackson Date Submitted: 7/21/69

APPROVED BY: W. S. STRUVE Date Released: 7/23/69

ABSTRACT
This report summarizes exploratory studies on improvements of humidity resistance of "Afflair", "Krolor" and quinacridone pigments. Substitutes for basic nickel carbonate (light stabilizing agent for QA pigments)and calcium Staybelite (texture agent) are being evaluated by exterior exposure.

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I. INTRODUCTION

The growing importance of humidity resistance testing for automotive finishes has imposed greater demands on our pigments. Several of our major products were deficient in this characteristic. These include representatives of our QA, CPC, and "Krolor" lines and all of our "Afflair" pigments.

These studies were designed to aid in overcoming this problem and were carried out simultaneously with work by B. J. Godfrey, C. W. Manger, and R. F. White and others.

II. SUMMARY AND CONCLUSIONS

A. "Krolor" products of apparently acceptable humidity resistance levels are being manufactured utilizing the Emery 3554D/Igepal CO710 texture treatment in place of calcium Staybelite, coupled with better washing. This results in a high level of humidity resistance in acrylic systems and acceptable performance in plastics. Alkyd gloss levels are degraded by this operation. (See KO-789, KY-788-D, KY-795-D.)

B. A well-washed, unextended quinacridone maroon, RT-920-D, 59160, has been prepared and submitted to the trade for use in humidity resistant systems (see R.F.White "Monastral" Maroon, RT-920 Check List dated 1/16/69).

C. Cobaltous oxalate extended QA's are on exposure in acrylic systems. This material does not degrade humidity resistance as does basic nickel carbonate.

D. Various metallo organic and inorganic extenders are being studied as potential replacements for calcium Staybelite in QA and CPC pigments.

E. Samples of A-133-D and A-36-D have been submitted to F. and F., Flint, as humidity resistance stabilizers. No reply on these has been received.

F. Some improvement in "Afflair" humidity resistance has been accomplished by SiO_2 coatings. This work is receiving further study.

III. PATENT STATUS

A. Patent coverage of the Emery/Igepal CO710 system is probably precluded by public use (KO-789-D) and chrome yellows.

B. The patentability of cobalt oxalate and modified A-133-D for this purpose should be considered.

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IV. EXPERIMENTAL STUDIES

A. Humidity Resistance Studies on "Krolor" Pigments

Code	Expt.#	Treatment		Result
KO-789	1877-34	Calcium and zinc Staybelite treatments.		Markedly degrade resistance in "927" lacquer.
KY-781-D	1877-51	A. Untreated control	All washed to 6000 ohms/cm^2	Control (excellent)
		B. Emery 3554/Igepal CO710 (low)		VVS ws
		C. Emery 3554/Igepal CO710 (high)		Vsl ws
		D. Neofat 10		Ws
		E. Dow-Latex (Styrene)		Sl better
		F. Petroleum sulfonate (low)		Vvs ws
		G. Petroleum sulfonate (high)		Sl ws

Conclusion: Well-washed "Krolor" (without calcium Staybelite treatment presents no problem of humidity resistance. None of the surface treatments applied benefitted the humidity resistance properties. All treatments were satisfactory for thermal stability and abrasion resistance in plastics.

KY-781	1877-59	Emery 3554D/Igepal CO710	Treatment plus washing to 4500 ohms/cm^2 excellent humidity resistance and abrasion resistance in polystyrene.
KY-781	1877-60	Further study of Dow-Latex Emulsion DL860 from 68-90% "Krolor" showed this polystyrene treatment rendered pigment incompatible with "927" lacquer system.	
KY-787	1877-62	Emery Igepal treated slurry ex. plant lot KY-787, 59885 (after SiO_3-acid treatment) coagulate with $Al_2(SO_4)_3$ and treat. Wash to 6000 ohms/cm^2. Resulted in excellent abrasion and humidity resistance properties (much superior to KY-787-D, TS-91005). This product is presently manufactured as KY-795-D. (The work on scale-up was done by R.F.White).	

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KY-781	1877-64	Non-organically treated "Krolor" filtered and washed to 6000 ohms/cm^2 shows excellent humidity resistance in "927" lacquer. Gloss levels are lower than the Emery 3554D/Igepal CO710 treated counterparts.

Overall Conclusions

In the opinion of the writer, all "Krolor" products for use in acrylic lacquer should be made with an Emery 3554D/Igepal CO710 treatment coupled with washing to an 6000 ohms/cm^2 endpoint (similar to KO-789-D). This treatment is satisfactory for use in plastics applications.

Products made in this manner are lower in gloss in alkyd systems than calcium Staybelite-treated counterparts. Further attempts should be made to develop a surface treatment that would increase dispersibility and gloss levels without harmful effects on humidity resistance.

B. Studies on humidity Resistance of "Afflairs"

"Afflair" pigments evidence very poor humidity resistance characteristics in "927" acrylic lacquer systems. Simple improvements such as better washing to remove electrolytes do not appreciably benefit this product type as it does "Krolor" or QA pigments. Several attempts have been made to alter this characteristic.

Reference

1815-63,70	Treat NF-123 and NF-133-D with various agents to (a) remove soluble salts, (b) alter basicity and acidity characteristics, (c) make pigment surface hydrophobic. Use of triethanolamine, $Na_4P_2O_7$, Emery 3554D/Igepal CO710, fatty acids, and petroleum sulfonates were studied. Sodium pyrophosphate treatment showed some benefit but to a very limited extent.
1815-70	Study of Empol 1040 (a highly polymerized carboxylic acid ex. Emery Industries) showed definite but inadequate improvement.
1815-71 1919K-2 1919K-11	SiO_2 deposition (as per "Krolor" type technique) upon the surface of "Afflair" pigments have shown some improvement in humidity resistance and gloss levels. These processes are receiving further study.
1919K-13	A study of the effect of sieve size of a given "Afflair "Afflair" (NF-133-D) showed interesting difference in behavior (i.e., larger particle size, lower gloss) and an unexpected result that humidity resistance was not effected by particle size.

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Reference

SW-00041 — Uncalcined "Afflair", stabilized by means of an iron pyrophosphate treatment, shows poor humidity resistance in "927" lacquer.

C. Studies on the Effects of Inorganic Extenders

The finding by H. Matrick that the addition of ca. 10% A-133-D, SD-00122, via dry blending benefitted the humidity resistance of quinacridone in an "867" acrylic lacquer system is of considerable speculative interest.

Subsequent work by the writer illustrated that this beneficial effect was shown particularly by the standard lot #00122 in "926" lacquer and not by random lots of plant production. A study was undertaken to determine the reasons for this.

Reference

1815-64A-D — Study effect of varying $Fe^{+3}/P_2O_7^{-4}$ ratios. Conclusion: Increase in use of $Na_4P_2O_7$ resulted in A-133-D of inferior humidity resistance effectiveness in blends with RT-920-D, 59160 (100% "Monastral" Maroon toner - well washed). Quantities of $Na_4P_2O_7$ above 190 gr. mol $FeSO_4.H_2O$ were detrimental. Good performance was shown by lab samples A, B, C.

1815-64G — Reducing water solubility of product by treatment with $TiOSO_4$ (see KN-54-16,18) was beneficial to humidity resistance. This finding should be studied further.

1815-69 — A study of heat development of A-133-D at various $Fe^{+3}/P_2O_7^{-4}$ ratios showed no beneficial effects resulted.

SW-00064, DSN69-1 — This was an attempt to duplicate the excellent results shown by standard lot 00122. Semi-Works and laboratory-washed samples were processed and tested in "927" acrylic lacquer for humidity resistance effects in blends with RT-920-D. None were fully equivalent to lot 00122.

SW-00072, DSN69-1 — A second lot duplicating 1815-64A and differing from 00064 in strike temperature and $Fe^{+3}/P_2O_7^{-4}$ ratio was made. This material, when tested in "927" lacrylic humidity test, closely duplicated standard lot 00122 and reduced the discoloration tendency resulting from microblistering shown by RT-920-D. This lot, however, is still not fully equivalent to 00122 standard which remains unique. Subsequent tests on a new proposed standard lot manufactured in the plant (92517) showed it to improve RT-920-D but not to the extent of lot 00122. These materials have been placed on exposure in Exp. Ser. 69449.

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5 lbs. of SW-00072 were sent to Dr. S. Arora, Flint, Michigan in May, 1969. No report has been returned by F. and F. as of this date.

Table 1 summarizes analyses made on various products in an attempt to characterize the cause of these varying performances. The following conclusions may be reached:

1. Humidity resistance effects do not correlate with the degree of hydration of the A-133-D.

2. A high degree of correlation is shown with sodium ion content. This is probably also related to effectiveness of washing (Na_2SO_4 removal) and to the variable amount of $Na_4P_2O_7$ in solid solution (See KN-54-18).

3. Degree of crystallinity of A-133-D had no apparent correlation.

Table 1

Sample	Humidity R Resistance	Anhydrous Basis % Na	% SO_4	% Fe	% P_2O_5	"As Is" % H_2O	% Na	% SO_4	% Fe	% P_2O_5
00122	Control	.44	.068	29.6	47.25	20	.35	.0545	23.63	37.8
1815-64A	=	.39	1.74	29.9	47.25	17	.32	1.44	24.85	39.2
1815-64D	much worse	1.71	.116	25.2	59.9	13	1.49	.101	29.92	44.3
00064D	Sl worse	.73	.242	27.8	48.8	15	.62	.205	23.63	41.5
00064E	Worse	.83	.403	29.15	49.7	18	.68	.331	23.39	40.8
58592	?	.61	.767	28.90	47.9	19	.49	.621	23.39	38.8
59897	Worse	.72	.464	28.15	47.2	21	.57	.367	22.17	37.3
60013	Worse	.89	.343	26.78	47.55	19	.72	.278	21.68	38.5

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Studies were made on other ferric phosphates as well as other metallic pyrophosphates.

Ref.		Effectiveness - "927" Lacquer
1815-64E	$Fe_5(P_3O_{10})_3$	Slight worse vs 100% RT-790-D
1815-64F	$FePO_4$	Slight worse vs 100% RT-790-D
1815-65	$Mn_2P_2O_7.Na_4P_2O_7xH_2O$ (A-22-D)	Worse vs 100% RT-790-D
1815-68	$Ni_2P_2O_7.Na_4P_2O_7xH_2O$	Slightly worse vs 100% RT-790-D

2. Substitutes for Basic Nickel Carbonate

Reference	
1815-67; 1901-16,17	The finding that basic nickel carbonate (N-947) dry blended or wet precipitated in presence of QA's degrades humidity resistance in "927" lacquer is very serious. This material is added to various QA's to aid in improvement of exterior light stability. A series of preparations were made from $NiCl_2$ and $NiSO_4$ varying the $Ni_2/CO_3^=$ ratio and also attempting to vary particle size. As anticipated, change in the anion did influence the result with $NiCl_2$ being the better source when coupled with lower amounts of $CO_3^=$. Increases in particle size apparently worsened the humidity resistant characteristics. 10% of 67A ($NiCl_2$ - low $CO_3^=$) resulted in only a very slight degradation of RT-920-D, 59160, versus the marked degradation shown by N-947. This approach could be taken if necessary for maximum light stabilization.
1919K-1	Nickelous phthalate was prepared and tested as a possible substitute for N-947. This material was unsatisfactory.
1919K-3	Ferrous and nickelous ammonium phosphates - unsatisfactory in humidity resistance.
1919K-4	Cobaltous ammonium phosphate - unsatisfactory in humidity resistance.
102-29 102-32	Cobaltous carbonate is a light stabilizer for QA pigments. Its humidity resistance is similar to basic nickel carbonate.

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1919K-4A — Cobaltous oxalate was found to be a satisfactory material for humidity resistance in "927" lacquer. Its light stabilizing action on QA pigments is being studied in Exp. Ser. 69449.

1919-4B — The corresponding nickelous oxalate was unsatisfactory.

1901-16 — Nickelous hydroxide harmed the humidity resistance of QA maroon.

3. Studies on Quinacridone Pigments

The need to eliminate clacium Staybelite from "Monastral" colors to improve humidity resistance is well established. Alternate treatments are being reexamined using compounds where durability data have been previously established, wherever possible.

Two principles are being tested: (a) render surface more hydrophobic, and (b) render surface more polar to improve dispersibility in system.

Reference

1910-15 — Series 1901-15 utilized approximately 10% of Emery 3554D/Igepal CO610; Neofat 10 (C_{10} Fatty Acid); Empol 1014 (C_{36} polymerized dicarboxylic fatty acid; and Empol 1040 (C_{54} polymerized tricarboxylic acid as a slurry treatment of "Monastral" Maroon presscake. All treatments were superior to calcium Staybelite in humidity resistance - none enhanced this property, i.e., all were equal to or worse than unextended control (RT-920-D-type).

1901-14 — Series 1901-14 was based on this approach, but employed the surfactants in the acid extraction of the dispersion-milled powder. This has given rise to an interesting result with Empol 1040, i.e., the humidity resistance was superior to unextended control. The mechanism of this superiority, i.e., it is due to particle size change, particle charge, i.e., Al salt of polymerized acid, effect on vehicle system (acing in manner similar to plasticizer, etc.) should be studied further.

1901-18 — "Monastral" Maroon extended with 7 to 22% of the aluminum salt of Empol 1040 showed diminishing benefit to humidity resistance as the extender was decreased. Rheology seems satisfactory versus RT-920-D, 59160. These products are being placed on exposure.

1901-44,53 — Surface treatment of "Monastral" Maroon and Maroon B with "Volan" and Volan L", DuPont methacrylato chromic chloride, showed the former made these pigments more humidity resistant. This approach is receiving further study.

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1901-48 SiO_2 coating of "Volan"-treated "Mcnastral" Maroon resulted in products of extremely poor humidity resistance.

4. Studies of Miscellaneous Metallo-Organic Type Extenders

Reference

1919K-6 Two forms of the aluminum salt of a petroleum sulfonate were proposed as possible extenders for use in QA's to improve texture. Aluminum petroleum sulfonate coagulated with Armac T seems to be satisfactory. Further study via precipitation in the presence of QA's or CPC's should be undertaken.

1919K-11 An attempt to improve the gloss level and humidity resistance of "Afflair" NF-133-D, by precipitation of the aluminum salt of Empol 1040 (polymerized tricarboxylic acid) showed only very slight improvement. This should be studied further since the humidity resistance level of NF-133-D is extremely poor.

1919K-15 Precipitation of the 'Al salt of DAXAD-11 showed small but significant improvements on NF-133-D.

5. Studies of Organic Surface Coatings

Reference

1919K-16 Attempts are underway to polymerize polymethyl methacrylate on the surface of "Afflairs". Preliminary results indicate PMM was applied to surface (rendering it hydrophobic). This lead is being currently studied.

6. Miscellaneous Inorganic Extender Studies

Reference

1815-66 $Mn(OH)_2$ is a good light stabilizer for QA pigments. This material was found to be unsatisfactory in humidity resistance.

1901-P-52 (SW-00023) A-36-D (85 mol % Cr^{+3}/15 mol T Fe^{+3} OH_3. This highly durable grey transparent extender showed good humidity resistance properties. A sample was submitted to F. and F. for evaluation. To date, no reply has been received.

1901-P-53 F-115-D, extremely small, well-washed ferric hydrate, has no effect on humidity resistance in blends with RT-920-D.

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For purposes of record, work by others has shown harmful effects from admixture of Blanc Fixe ($BaSO_4$), $Al(OH)_3$, and aluminum benzoate in this application.

Chromic petroleum sulfonate extensions of CPC blue or green (G-446, G-798) show excellent humidity resistance in TEA 3 lacquer.

The base material, unextended, was found to degrade the humidity resistance of "927" type lacquer.

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