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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

REACTIVITY OF $5NO_2 2NH_2$ ANISOLE → NAS-D (RT-588-D)
THE EFFECT OF SOLVENT TREATMENT

Period Covered: April 22, 1949 - March 15, 1950

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: REACTIVITY OF $5NO_2 2NH_2$ ANISOLE → NAS-D (RT-583-D)
THE EFFECT OF SOLVENT TREATMENT

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INTRODUCTION

One of the unfortunate properties of RT-588-D is its reactivity in a good many alkyd vehicles. Considerable work has been done by the General Organic Group in modifying RT-588-D in some manner to produce a less reactive product, particularly in a special Cook alkyd vehicle. Out of this work a modified pigment, RT-611-D, was produced which achieved its improvement in reactivity through additives.

This report points to another approach in achieving a less reactive product. The approach is based on the concept that the degree of reactivity, in addition to being a function of the surface area of a crystallite, is also a significant function of the physical state of the surface. The forces of attraction between the crystal surface and the constituents of the vehicle, which is responsible for the reactivity of the paint system, can be considerably altered by simply changing the nature of the crystal surface. What constitutes this change is not clearly understood, but it probably has to do with the degree of strain and crystal imperfection existing at the surface and perhaps to a lesser degree relates to the crystal habit.

The nature of the crystal surface can be changed through solvent action and this report deals with the effect that two solvents, chloroform and acetic acid have on the reactivity of RT-588-D. A previous memorandum report, RLM-49-42, also deals with the effect of solvent treatment on RT-588-D.

The concept of solvent action directly on the pigment to produce some desirable change in the nature of a pigment surface is one capable of opening up a large field for practical research.

SUMMARY AND CONCLUSIONS

1) Solvent treatment ($CHCl_3$ or HOAc) of RT-588-D, followed by a grinding step, is capable of producing a product of particle size smaller than that of the original pigment but of less reactivity.

2) This solvent treatment does not cause a phase change although with proper solvent treatment a phase change can be produced. See RF-49-19.

3) All solvent treated products have been somewhat on the dull side of RT-588-D and RT-611-D.

4) The solvent treated products of large particle size have been far superior in reactivity to either RT-611-D or RT-588-D, whereas the solvent treated products that have been ground to a small particle size have shown less reactivity than RT-588-D but more reactivity than RT-611-D in the Cook alkyd vehicle.

5) Even though the large particle-sized products are very low in reactivity, their opacity makes them unsuitable for use in metallics.

6) The concept of a pre-solvent treatment to affect reactivity is a very worthwhile one and there is opportunity for considerably more work in achieving proper control of the solvent on the pigment.

EXPERIMENTAL DISCUSSION

Samples of RT-588-D standard were exposed to chloroform or glacial acetic acid in various ways. After exposure, the slurries were not filtered but the solvent was evaporated at moderate temperature (never above 140°F.). This technique never removed anything from the pigment, hence any physical change could be attributed directly to the action of the solvent. Table I serves to illustrate the effect of this solvent exposure on the specific surface measurements by nitrogen adsorption.

TABLE I

EFFECT OF SOLVENT TREATMENT OF RT-588-D ON SPECIFIC SURFACE

Sample No.	Description	Sp. Surface (Sq. Meters/gram)
1	RT-588-D "as is"	52.8
2	Refluxed 2 hrs. in chloroform	9.5
3	" 8 hrs. in "	1.7
4	Soak 2 days in chloroform	9.8
5	" 8 " " "	6.0
6	Reflux 86 hrs. in chloroform & Ballmill 3-1/2 days in chloroform	6.7
7	Reflux 84 hrs. in acetic acid & Ballmill 3-1/2 days in acetic acid	6.8

It can be seen by reference to Table I, that even an exposure of 2 hrs. to boiling $CHCl_3$ very markedly increases the particle size to a point where the specific surface drops from 52.8 to 9.5 sq. M/g. It may also be seen that ballmilling this pigment in $CHCl_3$ or HOAc did not produce a specific surface any greater than around 6.8 sq. M/g. Also $CHCl_3$ and HOAc are equally effective in decreasing the specific surface.

Not all of the samples of Table I were examined tinctorially or for reactivity because it rapidly became apparent that no pigment of this type with a specific surface as low as 9.5 sq. M/g could be sufficiently intense or transparent in masstone to produce satisfactory metallic finishes. Two of the samples so examined, sample No. 6 and 7, when mixed with 10% RT-617-D, had considerably less reactivity in the Cook alkyd vehicle than RT-611-D as may be seen by reference to Table II.

TABLE II

	Ford Cup Readings (Sec)				
Age of Enamel (Days) →	Initial	4	7	14	30
*Sample No. 6 + 10% RT-617-D Lot 65802	18	25	25	32	47
" No. 7 + 10% " "	16	21	21	24	35
RT-611-D SD-66136	19	31	36	37	150

*Sample numbers refer to Table I.

Tinctorially, sample 6 and 7 were dull and showed up poorly in metallics due to their opacity when compared to RT-611-D.

Sample No. 2 was also examined without admixture with RT-617-D. This sample showed considerably less reactivity in the Cook vehicle than RT-688-D but it was inferior to RT-611-D. This is shown in Table III.

TABLE III

	Ford Cup Readings (Sec)			
Sample Age of Enamel (Days) →	Initial	4	7	30
#2 of Table I	22	35	40	60
RT-688-D, SD-65605	26	110	96(Thix)	190
RT-611-D, SD-66136	22	27	23	36

Here again, tinctorially, the sample was on the dull side and too opaque to show up well in metallics when compared to either RT-688-D or RT-611-D.

The above data seem to point directly to the statement that to decrease reactivity it is necessary to decrease the particle size but, in so doing, the pigment suffers so tinctorially that this method of reducing reactivity can never be practical. That this statement is not true is shown by the following experiment.

To obtain enough sample for this experiment, samples 6 and 7 (Table I) were combined. They had been given similar treatments but with different solvents. Their specific surfaces were about the same; their reactivity and their tinctorial properties were about the same. This sample which will be designated (6 + 7) was ballmilled for 72 hrs. using Nat OH/H_2O 50/50 as the liquid. In addition, RT-688-D was also ground under similar conditions. Specific surface measurements, and reactivity measurements were obtained. Table IV shows the results.

TABLE IV

	Reactivity in Cook Alkyd Vehicle Ford Cup Readings(Sec.)					Sp. Surf. Meas.
Age of Enamel (Days) →	Initial	2	7	24	120	sq. M/g
RT-611-D	19	22	24	42	182 (Thix)	-
RT-688-D	66	93	111	190	too hvy.	52.8
#6 + 7 Ground	40	50	58	70	115 (Thix)	52.1
RT-688-D Ground	106	101	207	195	too hvy.	55.6

*Numbers refer to sample numbers of Table I.

It can be seen from Table IV that ballmilling in the MeOH/MgO mixture reduced the particle size to less than that of the original pigment. The original pigment had a specific surface of 52.8 sq. M/g whereas the ground samples had specific surfaces greater than 80 sq. M/g. The important observation to make from Table IV, however, is that even at the high specific surface of 82.1 sq. M/g, the solvent treated material has less reactivity than the sample of comparable specific surface 88.6 sq. M/g. The only difference between the two samples is that one was given a pre-solvent treatment. This pre-solvent treatment did not add or subtract anything from the pigment. The pre-solvent treated sample of specific surface 82.1 sq. M/g is also better in reactivity than "as is" RT-688-D of specific surface 52.8 sq. M/g. This completely disproves any thoughts that one may have that the most important single consideration when dealing with the degree of reactivity of a single pigment is the specific surface. One must also give considerable consideration to the physical state of that surface. From Table IV it can also be seen that good as the solvent treatment and grinding may be, it does not yield a pigment as good as RT-611-D, but it must be remembered that the solvent treated and ground product contains no additives as does RT-611-D.

Even though the ground products give acceptable "flash" in metallics, both metallics and masstone are still on the dull side tinctorially when compared to RT-611-D or RT-688-D. It is not clearly understood why this should be so for a pigment of specific surface above 80 sq. M/g. Perhaps a specific surface around that of the original pigment will yield the optimum intensity. Particle size distribution may also play an important role in establishing the intensity of the masstone. It is felt that the control of particle size and particle size distribution of this pigment is a major undertaking in itself and no work other than what has been reported here has been attempted. It should be recalled (Table I) that the early and only attempt at such control through solvent exposure brought to light the fact that the particle size increased very rapidly with even mild exposure to solvent, making any precise control very difficult. Considerably more work will have to be done to obtain proper control through solvent action and the concept of the control of particle surface through solvent action opens up a large field of research.

An index of notebook references dealing with the work described in this report may be found in N.B. 1285 p. 132.