

151
E. I. DU PONT DE NEMOURS & COMPANY
PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
CHEMICAL DIVISION - COLORS
Final Report

FLOCCULATION RESISTANT PHTHALOCYANINES
PATENT EVALUATIONS

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

FLOCCULATION RESISTANT PHTHALOCYANINES
PATENT EVALUATIONS

FEB. 1951 - APRIL, 1953.

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SUBMITTED BY: *A. J. Stratton* 8/3/53
A. J. Stratton

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APPROVED BY: *J. H. Cooper* 7/9/53
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INTRODUCTION:

The following three patents have been given some evaluation in the laboratory and a limited amount of exploratory work was done along lines suggested by these patents:

U.S. 2,524,672 - Lecher et al - American Cyanamide
U.S. 2,526,345 - Giambalvo - Interchemical
U.S. 2,540,775 - Bronillard &
Giambalvo - American Cyanamide

SUMMARY AND CONCLUSIONS:

Two processes described in U.S. 2,524,672 and in U.S. 2,540,775 have not given results of any economic value with respect to flocculation resistant phthalocyanines. On the other hand, U.S. 2,526,345 which covers the use of copper phthalocyanine monosulfonic in mixtures with copper phthalocyanine has given substantially flocculation-free products. Subsequently, a program of research was undertaken which culminated in the release of two colors on June 1, 1953 (BP-366-D and BT-373-D). These are offered to the trade as flocculation resistant products. This work will be reported elsewhere. Such products are believed to come within the broad claims of U.S. 2,526,345, and DuPont now has a license to use this patent.

This experimental work at Newark has also led to the preparation of three patent proposals of our own which are being considered by the Legal Department for filing.

EXPERIMENTAL DETAILS:

U.S. 2,524,672 shows a process for preparing salts of phthalocyanine pigments by suspending them in a liquid and then adding a strong acid which is soluble in the suspending liquid. Example 1 was evaluated in Exp. 1424-49 by suspending CPC-LB and Cl-free CPC crudes in nitrobenzene and adding xylene sulfonic acid. There appeared to be complete salt formation. After 2 hours stirring, the salt was hydrolyzed with ethyl alcohol and the pigment filtered and washed with alcohol. It was finally steam distilled to remove residual nitrobenzene. The CPC-LB was about 20% weak vs BT-304-D and the Cl-free CPC was much weaker and had the appearance of a completely crystalline product. Flocculation tests were not run, but the process has little possibility of economic interest. A more practical example would have been the combination of sulfuric acid with nitrobenzene, and such products might be worthy of study at a later date.

U.S. 2,526,345 shows mixtures of CPC monosulfonic acid and CPC to give non-flocculating compositions. The preparation of CPC monosulfonic acid, after the disclosure of this patent, was done in Exp. 1393-32, though the heating cycle was not followed exactly. Sulfur analysis of the resulting product indicated that it contained only about 30% CPC monosulfonic acid. It was a weak, dull and greenish product by both rubout and enamel tests. However, mixtures containing 10% of this product and 90% BT-304-D gave enamels which were quite free of flocculation and appeared strong and intense vs BT-304-D. The interesting properties of this mixture resulted in

an extensive line of research which has led to the development of a new product comprising a co-synthesized mixture of CPC-LB and CPC-4-monosulfonic acid. This has been released as a rosinated lake, BP-366-D.

This patent shows the preparation of CPC-monosulfonic acid by direct sulfonation, but it can also be prepared by synthesis from a mixture of phthalic anhydride and 4-sulfophthalic acid. This route has been explored by Orchem and a mixture substantially as contemplated by Giambalvo has also been developed both by Orchem and by the Pigments Department. (BF-373-D).

The question of the validity of U.S. 2,526,345 was explored with the Legal Department, particularly in view of U.S. 2,285,359 which discloses the use of 4-sulfophthalic acid in mixtures with phthalic anhydride to give asymmetric compounds containing 1, 2 or 3 sulfonic acid groups per phthalocyanine molecule. The final conclusion was that U.S. 2,526,345 must be considered valid. Accordingly, a license agreement has been concluded with Interchemical for use of this patent.

Incidentally, U.S. 2,285,359 is owned by General Aniline and is included in an existing royalty-free license exchange.

U.S. 2,540,775 was evaluated in Exp. 1393-27. Essentially, this patent contemplates stirring a water slurry of CPC with a solvent such as carbon tetrachloride or toluene for several hours, followed by removal of the solvent by steam distillation to obtain a product which has high resistance to flocculation. The products treated were (1) acid pasted chlorine-free CPC, (2) salt milled chlorine-free CPC, and (3) solvent milled CPC-LB. By rubouts, the chlorine-free products were both weak against their controls, whereas the CPC-LB was unchanged. In alkyl enamels none of the products were free from flocculation. However, the CPC-LB was definitely improved and also appeared strong and intense vs its untreated control. The acid pasted CPC flocculated badly both before and after treatment, although the treatment seemed to give a slight improvement in strength. The salt milled Blue R also was improved slightly in strength, and there was very little flocculation either before or after treatment.

As a means of obtaining flocculation resistant CPC, this process does not appear attractive either from the economic or the operating points of view. However, this patent is quite broad in its claims as to treatment of phthalocyanine pigments with solvents and needs further review as to its relation to more recent processes on direct pigmentary products.

The evaluation of these patents also led to limited studies on other methods of preparing flocculation resistant phthalocyanines. In 1393-68 CPC polysulfonic acid ("Pontamine" Fast Turquoise 86L) was added to a water slurry of CPC-LB and precipitated with BaCl_2 to give a substantially non-flocculating CPC toner. This was later modified to include precipitation with aluminum sulfate instead of BaCl_2 and was coded BT-345-D. For a combination of policy and economic reasons, this product has not been released for sale.

In a similar manner, separately prepared lakes of CPC-Poly-sulfonic acid were tested in mixtures with CPC-LB in alkyd enamels for flocculation resistance, but nothing of interest came of these tests. On the other hand, two CPC sulfonamides prepared at Jackson Laboratory, were tested in mixtures with CPC-LB, and one of them gave a definite improvement in flocculation. Although the other one showed no improvement, it was so impure that no conclusion as to its usefulness should be drawn.

Other work not included in this report has also demonstrated that a co-synthesized mixture of CPC-LB and a CPC containing free carboxy groups (perhaps they are actually amide groups, $-\text{CONH}_2$) is also resistant to flocculation. In view of these interesting results and the state of the art as described in RLM-52-4, three patent applications have been proposed and are in the hands of the Legal Department for filing.

1. The mixtures obtained by precipitating a metal salt of CPC Polysulfonic acid on CPC.
2. The preparation of mixtures of CPC and CPC monosulfonic acid, not exceeding about 15% of the latter, by co-synthesis from mixtures of phthalic anhydride and 4-sulfo phthalic acid.
3. A broad case covering the use of other polar groups such as $-\text{SO}_2\text{NH}_2$, $-\text{CONH}_2$, $-\text{P}(\text{OH})_2$ and their derivatives to promote flocculation resistance.

The above work is recorded in notebooks 1393 and 1424.

MPH