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E. I. DuPont de Nemours & Company

Jackson Laboratory

May 25, 1942

DuPont Naphthanil Orange GC 50 Base

(meta-Chlor-aniline-hydrochloride + maleic acid)

JLR 38-57, No. 1 Serial Number 18054

E. I. DuPont de Nemours & Company

Jackson Laboratory

Azo Colors Division

S. S. Rossander

Progress Report

May 25, 1942

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(meta-Chlor-aniline-hydrochloride + maleic acid)

Group Leader - C. E. Sparks

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Reported By - C. E. Sparks

Work Started - March 1, 1941

Completed - May 1, 1942

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DuPont Naphthanil Orange GC 50 Base
(Project Number 2165)

C. E. Sparks

JLR-38-57, No. 1 Serial Number 18054

Object of the Investigation:

To develop a Naphthanil Orange GC 50 Base which possesses satisfactory storage stability and printing paste stability.

Period Covered by the Report:

March 1, 1941, to May 1, 1942.

Historical Background:

Lot 1 of DuPont Naphthanil Orange GC 50 Base (1500 pounds) was found to be satisfactory by our Technical Laboratory versus Jackson Laboratory Final Sample J-38-F-106. After approximately 2 and 1/2 months' storage at the Technical Laboratory (temperature 75-80°F.), it was noted that the sample had deteriorated slightly due to the presence of an insoluble product in the diazo solution Material stored in the shipping house (temperature about 50-55°F.) was found to be satisfactory with only a trace decomposition. Titration of the deteriorated sample to standard nitrite indicated no noticeable decomposition. In view of the difference in the decomposition rates between the material stored in the shipping house and at the Technical Laboratory, it was requested that the Naphthanil 50 Bases be stored in the coolest possible place at the Dye Works. (See letter of February 24, 1941, of C. E. Sparks to J. J. Carrigan.) It was decided, however, that Jackson Laboratory should attempt to obtain an Orange GC 50 Base which is stable to storage. In order to accomplish this, a special project J-38-57 was taken out for this work. This report summarizes the work done in this connection.

Conclusion:

A completely satisfactory DuPont Naphthanil Orange GC 50 Base with reference to storage stability and printing paste stability has not been found.

Summary:

DuPont Naphthanil Orange GC 50 Base (meta-chlor-aniline-hydrochloride + maleic acid) deteriorates slowly on storage at

room temperature; a reaction taking place which, on the basis of chemical analysis appears to be the formation of a maleate of meta-chlor-aniline of a molar ratio of 1.56 meta-chlor-aniline to 1 of maleic acid. This reaction product is insoluble when Orange GC 50 Base is diazotized. The decomposition of Orange GC 50 Base after 16 months' storage on the Dye Works cannot be determined by nitrite analysis. No satisfactory method of preventing the reaction of meta-chlor-aniline with maleic acid has been found.

The cloudy appearance of the diazo of Orange GC 50 Base which has been stored for several months at room temperature does not in any manner change the shade and strength on printing of the product.

Patent Situation:

A patent application has been filed (Rossander, Sparks, and Maynard Case I - Serial Number 358,296) which protects Naphthanil Orange GC 50 Base.

No additional patentable material has been discovered in the investigation reported herein.

Plans for Future Work:

Work will be concentrated on obtaining a satisfactory Naphthanil Blue B 50 Base and leads obtained from this investigation will be applied to the Orange GC 50 Base, since the possible sales of the latter product are small as compared to the Blue B 50 Base. Also the storage stability of Blue B 50 Base is very much inferior to the Orange GC 50 Base.

Experimental:

The experimental work covered during the period of this report can be found recorded in the following Jackson Laboratory Notebooks: 3436, 3504, 3536, 3634, 3843, 3648.

Nature of the reaction between meta-chlor-aniline hydrochloride and maleic acid

The reaction occurring between meta-chlor-aniline-hydrochloride and maleic acid proceeds with very slow velocity at room temperature. Storage of Lot 1 of Naphthanil Orange GC 50 Base (mixed in December, 1940) until April, 1942, at room temperature contained a very small amount of insoluble matter

matter in the diazo solution. From 800 g. of such material there was obtained only 7 g. of insoluble matter whose analysis showed it to be a mixture of meta-chlor-aniline maleate of molar ratio 1.56 meta-chlor-aniline to 1 maleic acid. There was no titratable loss of diazotizable meta-chlor-aniline during this 16 months' storage of Lot 1 at domestic shipping house. The only noticeable change was the development of a small amount of turbidity in the diazo solution. The shade and strength of Lot 1 are satisfactory versus a specially prepared fresh mix.

It has been definitely shown that heat accelerates this reaction. Preliminary tests indicate that moisture also accelerates the reaction. The presence of maleic anhydride definitely accelerates the reaction.

Substitute for Maleic Acid

In order to obtain an Orange GC 50 Base which was more stable to storage, certain materials were investigated as possible substitutes for maleic acid. The following table summarizes briefly the reagents tried in this connection:

TABLE I

Substitutes for Maleic Acid in Naphthanil Orange GC 50 Base
(Orange GC Base + diluent 1:1)

Substitutes	Printing Paste Stability	Oven Stability at 50°C.
1-Sulfo-naphthalene	heavy shades - 5 light shades - 1	
1-Sulfo-naphthalene potassium salt	heavy shades - 4 light shades - 3	
Mixture of p-tolyl-sulf-toluene and maleic acid 1:1	4	Inferior
3,5-Disulfo-nitro-benzene + maleic acid 1:1	4	Inferior
2,7-Disulfo-naphthalene sodium salt + maleic acid 1:1	4	Inferior
1,3,6-Trisulfo-naphthalene sodium salt + maleic acid 1:1	4	Inferior
Sugar + maleic acid 1:1	5	Inferior
Na_2SO_4 + maleic acid 1:1	5	Sli. superior*

* Sodium acid maleate ppts. in diazotization.

Code: 5 - equal to standard 50 Base
4 - slightly inferior to standard 50 base
1 - inferior to Orange GC Base

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See JLR-38-D, No. 21; S.N. 17983 and JLR-38-V-23, No. 1 for reagents other than maleic acid which have been evaluated as printing paste stabilizers for DuPont Naphthanil Orange GC Base.

meta-Chlor-aniline-sulfate

A sample of meta-chlor-aniline-sulfate was prepared by the reaction of sulfuric acid (monohydrate) on a toluene solution of meta-chlor-aniline. The resulting precipitate was filtered and dried. Mixtures of meta-chlor-aniline-sulfate and maleic acid were evaluated in the Naphthanil 50 Base versus Naphthanil Orange GC 50 Base (meta-chlor-aniline-hydrochloride + maleic acid). Storage stability tests indicated that the sulfate had no advantage over the hydrochloride for stability and was equal in printing properties both for shade, strength, and printing paste stability versus the standard 50 base.

The effect of moixture upon the decomposition of DuPont Naphthanil Orange GC 50 Base

Samples of Orange GC 50 Base containing a small amount of water (2-3%) were found to decompose quite rapidly when stored in an oven at 50°C. Samples of Orange GC 50 Base prepared by mixing (5 and 10%) partially dehydrated aluminum sulfate, anhydrous magnesium sulfate, and Zelan A with maleic acid and meta-chloro-aniline hydrochloride showed no advantage in storage stability over the standard mix.

Effect of reducing agents on Orange GC 50 Base

Samples of Orange GC 50 Base containing 5% sodium hydrosulfite were stored, stoppered, and unstoppered, at 50°C. and at room temperature. Storage tests indicated that the effect of sodium hydrosulfite on the stability of Orange GC 50 Base was negligible.

It will be noted from the above results that we are not clear as to exactly what promotes the reaction between meta-chlor-aniline-hydrochloride and maleic acid. It is believed

that moisture and heat are the two greatest accelerating agents. We do not believe that the storage stability of Orange GC 50 Base is sufficiently serious to be too much concerned with at the present time in view of the small sales. Work on the 50 Base problem is to be concentrated on the preparation of a satisfactory Blue B 50 Base for the time being, hoping that information obtained may be transferred to Orange GC 50 Base.

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fmb
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