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Jackson Laboratory

May 2, 1945

Naphthanil G (Diaceto Acetyl-o-Tolidine) and Diagens Therefrom

Progress Report

B. G. Carson

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Division Head

Serial Number 18785 JLR-38-60, No. 1

DUP050040879

Naphthanil G (Diaceto Acetyl-o-Tolidine) and Diagens Therefrom

B. G. Carson

JLR-38-60, No. 1 Serial Number 18785

Object of the Investigation:

To check the I.C.I. process for Brenthol AT, to prepare a final sample duplicating Naphthol ASG (General) and to prepare final samples of Diagens corresponding to (a) Rapidogen Yellow GS, (b) Rapidogen Yellow 2G, and (c) Rapidogen Golden Yellow 3R.

Period Covered by the Report:

September 8, 1943 to May 1, 1945

Historical Background:

In the development of a line of Naphthanils and Diagens no Naphthanil for yellows had been found with a substantivity equal to that of Naphthol ASG (General), di aceto acetyl-o-tolidine. With the expiration of the patent covering this coupling component the Sales Division indicated that its addition to our line of Naphthanils as well as the manufacture of Diagens made therefrom was desirable and requested the preparation of final samples.

Summary and Conclusions:

Final samples have been prepared duplicating in all essential details Naphthol ASG, Rapidogen Yellow GS, Rapidogen Yellow 2G, and Rapidogen Golden Yellow 3R. These duplications have been submitted to the Technical Laboratory as J-38-F-129, J-38-F-132 (also J-38-F-132B) J-38-F-131, and J-38-F-130 respectively.

A tentative Semi-Works Process S.N. 18785-A has been written for the manufacture of Naphthanil G. A tentative Chambers Works Process S.N. 18785-E for the recovery of xylene and acetoacetic ester and tentative Chambers Works processes (S.N. 18785-B, 18785-C, and 18785-D, respectively) for the manufacture of the New Diagen Yellows corresponding to J-38-F-130, J-38-F-131, and J-38-F-132 have been written.

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Two lots of approximately 3000 pounds each of Naphthanil G have been manufactured in the Semi-Works with yields of 93% and 89% respectively. No trouble in obtaining material of good quality was encountered in these productions. One lot of about 2000 pounds each of Diagen Yellow A2Y (Rapidogen Yellow 2G) and Diagen Yellow AY (Rapidogen Yellow GS) have been manufactured.

Trouble was encountered in obtaining sufficient greenness and brightness in the manufacture of Diagen Yellow AY. An examination of the authentic sample of Rapidogen Yellow GS (P.S.A. 17883) by Mr. H. W. Daudt showed that there was present a stabilized diazo compound of p-chloro-o-anisidine, along with the stabilized diazo compound of p-chloro-o-toluidine in the ratio of about 1:2. A new final sample, J-38-F-132 A, containing 10.85% Diagen A Base p-chloro-o-anisidine and 22.9% Diagen A Base p-chloro-o-toluidine with 24.5% Naphthanil G was reported to be trace green and trace bright versus the authentic Rapidogen Yellow GS. A complete report from the Technical Laboratory has not seen received on J-38-F-132-A.

It has been found that reducing the extent of the distillation during laboratory preparations of di aceto acetyl-o-tolidine materially increases the yield and reduces the necessity for purification of the acetoacetarylide. Diacetoacetyl-o-tolidine may be manufactured in nickel equipment.

Patent Situation:

See Anticipation Reports: AN-118, AN-2354, AN-2355, and AN-2356.

We are free to manufacture and to sell Naphthanil G and the herein described Diagens prepared therefrom.

Plans for Future Work:

Work is under way to prepare solutions of Diagen Yellow AY and Diagen Yellow A2Y. This work will be continued. At present it is believed that 20% solutions of Diagen Yellow A2Y have approximately the same degree of stability as the corresponding Pharmasol Yellow GN. It is hoped that this stability can be improved.

Experimental Work:

Naphthanil G: J-38-F-129

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Size of Laboratory Charges:

In all the laboratory condensations the charges were twice that of the I.C.I. process dated January 1942 expressed in grams. The amounts of reagents used were:

Tolidine	- 142 g.	- 0.67 mol.
Acetoacetic ester	- 346 g.	- 2.67 mol.
Xylene	-1100 g.	-
Soda Ash	- 6 g. or	2.2 g. 50% NaOH +8 cc. alcohol

Apparatus:

A 3-necked, 3-liter flask equipped with ground glass connections to a thermometer well, a dropping funnel, and a still head with a wier take-off was used. The heat was supplied by an oil bath containing two immersion heaters only one of which was thermostatically controlled. The agitation was supplied by the uaual half-moon agitator connected to the flask through a "Trubore" water-cooled bearing.

Variables Checked:

The effect of the following variables was determined: (1) order of addition, (2) type of alkali, (3) rate of heating, (4) extent of distillation during condensation, (5) rate of addition of reagents, and (6) effect of nickel on the condensation.

The exact character of the acetoacetic ester used was never determined. It was found early in the work that all the acetoacetic ester available was several months old. On the assumption that at least a small portion of it had decomposed to give a color deeper than "straw color" the supply was stirred for twenty four hours with a large quantity of anhydrous soda ash to remove both acidic products and water. This material appeared to be perfectly satisfactory. Freshly distilled material, on the other hand, even though distilling over a range of only a few degrees, was not satisfactory. It appeared that simple fractionation did not remove the deleterious products present. The color of the acetoacetic ester appears to offer no indication of its suitability for this preparation. Water-white material untreated with soda ash, though neutralized with soda ash or alcoholic caustic at the beginning of the reaction, might give tarry products varying from light yellow to dark brown. Dark colored material, pretreated with soda ash, might give pure white products requiring little or no washing

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with xylene.

The various laboratory runs are tabulated in the following tables, omitting two or three preparations in which the quality of ester used was questionable.

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Table I

Variable: Order of Addition

Run (JLNB-4181)	Reagent Added at 120°C.	Distillate	Time ater 140°C.	Grams Yield	% Yield	Color	Melting Range
125	Tolidine	600 cc.	105 min.	248	97.4	white	204°C.
127	Tolidine	600 cc.	100 min.	229	89.8	n. yellow	198-201
131	Ester	600 cc.	96 min.	208	81.6	Very yellow	?
136	Ester	550 cc.	89 min.	234	91.8	Very yellow	192-6
139	Ester	560 cc.	163 min.	215.5	84.4	white	200-6
140	Ester	500 cc.	105 min.	227	89.0	white	203-6

Discussion of Table I:

The average yield of runs 125 and 127 is 93.6%. The average of all the others is 86.7%. It is not believed that this difference has much significance.

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Table II

Variable: Type of Alkali

Run JLNB-4181	Alkali	Distillate in cc.	Time after 140°C.	Grams Yield	% Yield	Color	Melting Range
140	Soda ash	500	105 min.	227	89.0	white	203-6°C.
141	Alcoholic NaOH	550	130 min.	226	88.6	white	201-3°C.

Discussion of Table II

No significant difference is seen between the use of soda ash and the use of alcoholic caustic. The final product for run 140 undoubtedly contains soda ash while the run 141 probably does not. For all practical purposes, however, the two runs gave similar products.

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Table III

Variable: Rate of Distillation

Run (JLNB-4181)	Time for Distillation	Distillate in cc.	cc/minute	Grams Yield	% Yield	Color	Melting Range
129	99 min.	590	5.96	219	85.8	ap. yellow	198-200°C.
139	237 min.	560	2.36	215.5	84.4	white	200-6°C.

Discussion of Table III:

The rate of distillation appears not to be critical. The color difference between these two extremes in the rate of distillation may be attributable to slight differences in the purity of the ester or to the completeness of washing.

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Table IV

Variable: Rate of Addition of Reagent

Run JLNB-4181	Time (Min.) for Adding Reagent	Time for Distillation (Minutes)	Distillate (cc)	Time (min.) above 140°C.	Grams Yield	% Yield	Color	Melting Range	Remarks:
131	95	155	600	96	208	81.6	Very yellow	?	Purification not attempted.
136	4	176	550	89	234	91.8	Very yellow	192-6	
141	2	190	550	130	226	88.6	white	201-3	
140	2	190	500	105	227	89.0	white	203-6	
125	1	145	600	105	248	97.4	white	204	
127	1	133	600	100	229	89.8	Noticeably yellow	198-201	

Discussion of Table IV

The data of the above table indicates that the reagent added at 120°C. should be added quickly.

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Table V

Variable: Extent of Distillation

Run (JLNB 4181)	Distillate in cc.	Time (min.) above 140°C.	Grams Yield	Color	Melting Range	% Yield	Remarks
156	250	None	213.5	white	204-6°C	84.8	
157	194	1	235.0	white	206-9°C	92.2	Nickel agitator and nickel test strip present.
125	600	105	248.0	white	204°C	97.4	
127	600	100	229.0	Not. yellow	198-201	89.8	
129	590	59	219.0	Ap. yellow	198-200	85.8	
139	560	163	215.5		200-6	84.4	
143	250	21	246.5	white	202-4	98.6	
142	332	54	240.5	white	208-10	94.4	

Discussion of Table V:

Except for run 125 which appears to be a "freak" preparation for all the tables, it appears that the internal temperature of the condensation mass may be taken as an indication of the extent to which the reaction has proceeded. Runs 156, 157, 142, and 143 gave white products requiring little or no washing with xylene. In other runs (except 125) it was noticed that after the temperature reached 140°C the precipitated solids became progressively darker

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the longer the distillation proceeded. The presence of nickel has no bad effect on the product.

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Preparation of Final Sample, J-38-F-129:

JLNB 4181-144:

A composite sample made from the following laboratory preparations was micropulverized and tumbled overnight.

4181 - 136 - 234 grams, MR 192-6°C.
4181 - 138 - 168 grams, MR 195-200°C.
4181 - 139 - 215.5 grams, MR 200-6°C.
4181 - 140 - 227.0 grams, MR 203-6°C.
4181 - 141 - 226.0 grams, MR 201-3°C.
4181 - 142 - 240.6 grams, MR 208-10°C.
4181 - 143 - 246.5 grams, MR 202-4°C.
Total 1558.0 grams, MR 202-4°C.

The melting range of diacetoacetyl-o-tolidine is probably a better criterion of its purity than the analysis for purity by coupling. The composite sample before the addition of Alkanol B had a melting range of 202-4°C. as compared to 198-202°C. for Naphthol ASG, authentic product sample 23023. Its purity by coupling was 104.4% as compared to 102.8% for Naphthol ASG.

Preliminary samples containing (a) no wetting agent (b) 1% Alkanol, and (c) 1% Duponol ME Dry were submitted to the Technical Laboratory. The sample containing 1% Alkanol B was chosen as having satisfactory wetting-out properties; so a final sample consisting of 655 grams of the above composite sample and 6.6 grams of Alkanol B was mixed and submitted to the Technical Laboratory as J-38-F-129. The Technical Laboratory reported this procuct as being similar to Naphthol ASG.

Diagen Yellows

Analyses of Competitive Products:

Before attempting to duplicate the competitive Rapidogen Yellows they were analyzed for Naphthol ASG content and for stabilized diazo content calculated as the stabilized diazo compounds manufactured by DuPont.

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Rapidogen Yellow 2 G

Naphthol ASG - 30.4% (1.74 equivalents)
Diagen A Base p-chloro-o-anisidine (PCOA) - 28.4% (1.0 equivalent)

Rapidogen Golden Yellow 3 R:

Naphthol ASG - 17.4% (1.38 equivalents)
Diagen Base Dianisidine - 21.7% (1.0 equivalent)

Rapidogen Yellow GS:

Naphthol ASG - 22.4% (1.1 equivalents)
Diagen Base p-chloro-o-toluidine (PCOt) 4% (1.0 equivalent)

Preparation of Final Samples:

Best coupling ratios to duplicate the shades of Rapidogen Yellow 2 G, Rapidogen Yellow GS, and Rapidogen Golden Yellow 3 R were determined by the Technical Laboratory using as a coupling component part of the composite sample of Naphthanil G 4181-144 (J-38-F-129).

On the basis of these ratios Naphthanil G (J-38-F-129) was mixed with the appropriate finely ground stabilized diazo compounds by tumbling for two hours in a large aluminum mixer. Preliminary tests had shown that it was not necessary to add a wetting agent to the mixtures. Micropulverized sugar was used to adjust the strength.

The final samples of Diagen Yellows submitted had the following composition:

J-38-F-132 (Duplicating Rapidogen Yellow GS)

Naphthanil G - 26.5% (1.525E)
Diagen A Base PCOT - 27.8% (1.0E)
Sugar to make - 100.0%

J-38-F-131 (Duplicating Rapidogen Yellow 2 G)

Naphthanil G - 26.1% (1.915E)
Diagen A Base PCOA - 22.8% (1.0E)
Sugar to make - 100.0%

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J-38-F-130 (Duplicating Rapidogen Golden Yellow 3 R)

Naphthanil G	-	23.6% (1.97E)
Diagen Base Dianisidine	-	20.6% (1.0E)
Sugar to make	-	100.0%

Analyses as A Means of Standardizing New Diagen Yellows

It was thought worthwhile to make a comparison of the percentage figures for these final samples as derived from (a) Competitive product analyses, (b) Technical Laboratory ratios, (c) Analyses of components before mixing, and (d) actual analysis.

Table VI

Comparison of Compositions

Product Analyzed	Naphthanil G	Diazo
Rapidogen Golden Yellow 3 R	17.4%	21.7%
Each Component	24.1	20.0
T. L. Ratio	23.7	19.6
J-38-F-130, direct analysis	23.6	20.6
Rapidogen Yellow 2 G	30.4	28.4
Each component	22.0	26.1
T. L. Ratio	24.4	28.4
J-38-F-131, direct analysis	22.8	26.1
Rapidogen Yellow GS	22.4	32.4
Each Component	25.4	28.7
T. L. Ratio	23.2	26.3
J-38-F-132, direct analysis	26.5	27.8

From the above comparison it would seem that adjusting a mixture to a definite percentage basis by analysis, confirmed by printing tests would be a satisfactory method of standardizing these products. The small differences between the percentages in any group appears to be within the range of analytical or printing accuracy. J-38-F-132 was judged to be 10% weak by printing. Increasing each component of the sample by 10% would have the effect of bringing the percentages within reasonable agreement with those of Rapidogen Yellow GS.

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Second Final Sample of Diagen Yellow AY J-38-F-132 B

After Mr. H. W. Daudt had found that Rapidogen Yellow GS contained about a third of its diazo amino compound as the stabilized diazo compound of p-chloro-o-anisidine, the Technical Laboratory was asked to make printings with Naphthanil G in which Diagen A Base p-chloro-o-toluidine was replaced by Diagen A Base p-chloro-o-anisidine to the extent of 15%, 20%, 25%, 30%, and 35%. These prints showed that a substitution of 30% of Diagen A Base p-chloro-o-toluidine by Diagen A Base p-chloro-o-anisidine gave prints trace green in heavy shades and trace dull in light shades. Increasing the amount of Naphthanil G in the printing mixture gave no improvement in shade. On the basis of these prints a mixture was made up consisting of the following:

Naphthanil G, Lot 2	-	208 grams
Diagen A Base PCOT, chg. 258 (85.7%)	-	226 grams
Diagen A Base PCOA, chg. 2, 82.9%	-	111 grams
Powdered sugar	-	225 grams
Total		770 grams

After mixing by tumbling for two hours a small sample was submitted for printing test and was found to be 10% strong versus Rapidogen Yellow GS (P.S.A. 23551). To 750 grams of the mixture was added 75 grams powdered sugar and the whole was tumbled for two hours more. The Technical Laboratory reported this product as being trace green, trace bright, with a strength of 95:100 versus Rapidogen Yellow GS (P.S.A. 17883).

Other Samples of Rapidogen Yellow GS

Four samples of Rapidogen Yellow GS, three authentic and one trade sample, have been available to the Technical Laboratory during this work.

P.S.A. 17883. This authentic sample was used as a standard in the examination of the first final sample (J-38-F-132) and also for standardizing Diagen Yellow AY Lot 2. Approximately one third the stabilized diazo compound in this sample was found to be stabilized p-chloro-o-anisidine.

P.S.A. 23551. This authentic product is noticeably red, noticeably dull versus P.S.A. 17883. Of its total diazoimino content approximately half is stabilized p-chloro-o- anisidine.

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No reason is apparent for the redness and dullness of this sample.

P.S.A. 23594. This authentic sample is similar to P.S.A. 23551. It was not examined for p-chloro-o-anisidine diazoimino content.

Submitted for Typing: September 20, 1945
Date of Typing: September 24, 1945
jed

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