18799 (FLR 56-46, Unit 1)

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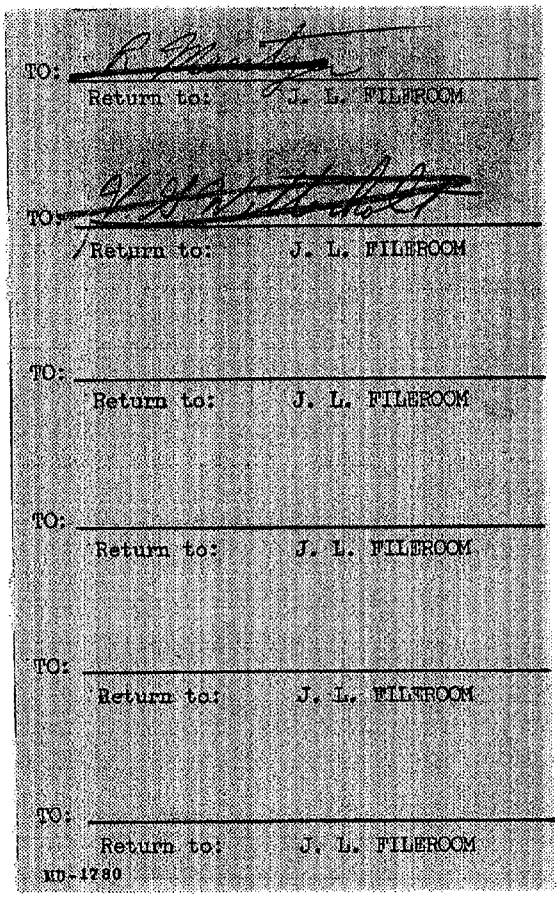

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JLR-56-46, No. 1.

Serial Number 18799.

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Jackson Laboratory

February 9, 1944

DuPont Anthraquinone Blue 3G

Problem Report

E. C. Buxbaum
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Written by - E. C. Buxbaum

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DuPont Anthraquinone Blue 3G
Wool Colors Process Studies
(Project No. 2431)

E. C. Buxbaum
R. C. Seyler

JLR-56-46, No. 1. Serial Number 18799.

Object of the Investigation:

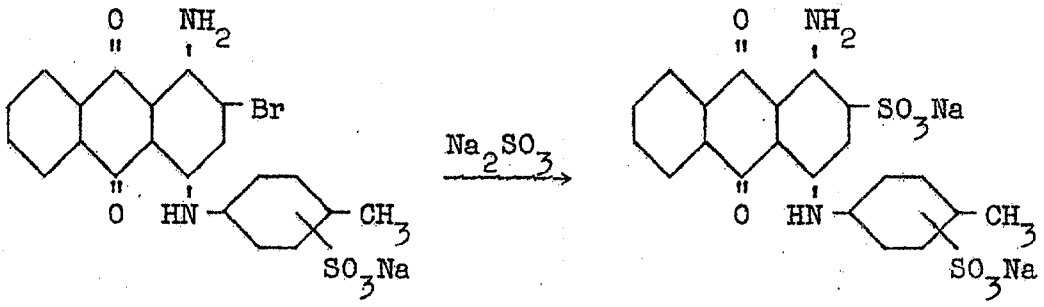
To study the manufacture of DuPont Anthraquinone Blue 3G in the plant and to investigate the process for its manufacture. Also, to suggest and recommend such changes in the process as are indicated from the study undertaken and which will facilitate the production of satisfactory color. Another object is to set up adequate tests and controls which will make the process easier and more accurate to operate under the conditions necessary to produce satisfactory DuPont Anthraquinone Blue 3G.

Period Covered by Report:

January 14, 1944 to February 2, 1944.

Historical Background:

DuPont Anthraquinone Blue 3G is prepared by sulfiting DuPont Anthraquinone Blue SKY at a temperature of 98-100° according to the following reaction:



DuPont Anthraquinone Blue SKY DuPont Anthraquinone Blue 3G

This color was developed in the Carrollville laboratory in 1930 and was first manufactured in the same year. The product was covered by U.S. 1,131,516 (Ref. 5) and the process was operated under a license from the Chemical Foundation until the expiration of the patent on March 9, 1932.

The first process for DuPont Anthraquinone Blue 3G was Plant Process A - Color 3181, dated August 17, 1930. This process used sodium bisulfite and sodium hydroxide and the alkalinity was

adjusted until a "faint pink coloration" on phenol-phthalein was obtained.

The second process was entitled "DuPont Anthraquinone Blue 3G" and was dated March 23, 1938. It was a Carrollville process. This was a revision of the previous process but no major changes were made.

Present production is being operated under "standing orders" dated January 7, 1944. These represent conditions somewhat different from the last process available which is the "Carrollville" process of March 23, 1938. No Dye Works process exists. Both processes prepare the sodium sulfite necessary to the reaction from sodium bisulfite and sodium hydroxide. The present standing order utilizes a volume almost twice that of the old Carrollville process. The sodium sulfite concentration is substantially the same but since our present volume is almost twice that formerly used, the amount of sodium sulfite used is almost twice as much as that used in the Carrollville process.

This work was carried out in the Ponsol area laboratory under a special arrangement designed to bring all processes for the manufacture of anthraquinone wool colors up to date and give operating experience on the revised processes. Under this arrangement Mr. Buxbaum representing the Jackson Laboratory and Mr. Seyler representing the Ponsol area laboratory will investigate all of the wool color processes and make such alterations and additions as found necessary to assure manufacture of standard colors. Mr. Buxbaum will write all progress or problem reports and Mr. Seyler will write the plant processes.

Conclusions and Recommendations:

The manufacture of DuPont Anthraquinone Blue 3G in the plant has been studied and the present process investigated.

The conversion of DuPont Anthraquinone Blue SKY to DuPont Anthraquinone Blue 3G depends for complete conversion on the proper pH, preferably, pH 9-10. Accurate control with a pH meter is to be preferred to indicator papers.

High pH results in poor conversion and a violet by-product while very low pH also results in incomplete conversion. The use of sodium bisulfite and sodium hydroxide makes it difficult to run this color on the night shift when adequate supervision to check pH may not be available. The use of sodium sulfite gives correct pH without adjustment and makes for simplified operation producing color equal to our present process.

Blue 3G in yields above process and of good quality can be obtained under proper pH control as evidenced by a run of five charges in the plant.

A new Dye Works process will be written utilizing the information obtained in this study. Adequate tests and controls for the manufacture of DuPont Anthraquinone Blue 3G have been devised. The objects of the investigation have been attained.

The following recommendations are made:

1 - If sodium bisulfite and sodium hydroxide are used, adjust the pH to 9-10 with a pH meter.

2 - Replace the use of sodium bisulfite and sodium hydroxide with sodium sulfite.

3 - Check the acidity of all Blue SKY cakes used for Blue 3G to avoid acid cakes which would reduce the pH making pH adjustment necessary.

4 - More emphasis on the maintenance of the proper temperature to avoid over long heating.

5 - Avoid the use of sub-specification sodium sulfite or bisulfite.

Summary:

The conversion of DuPont Anthraquinone Blue SKY to Blue 3G is dependent upon maintaining the proper pH during the sulfiting which should be pH 9-10. A pH less than 7.0 results in incomplete conversions while a pH of 11.0 or over is apt to result in insoluble, unconverted Blue SKY.

In the formation of sodium sulfite from sodium bisulfite and sodium hydroxide, the pH control should be done with a pH meter rather than indicator paper since the blue color of the solution makes it difficult to determine the proper endpoint.

A series of five charges of Blue 3G were run with controlled pH and resulted in complete conversions which yielded Blue 3G which was green and bright and gave an efficiency of 112.6% of process.

A study of the Carrollville process for Blue 3G which runs the conversion in half the volume used of the Dye Works shows that under these conditions, proper pH control is very important since the pH range in which complete conversion can be obtained is shorter

than that found for the larger volume and necessitates greater care. The present large volume provides a leeway which is desirable in the operation.

The use of sodium sulfite in place of sodium hydroxide and sodium bisulfite appears desirable from all points of view since the proper pH for conversion is obtained automatically.

Proper maintenance of temperature is very important as lower temperatures make for incomplete conversions. Higher alkalinity results in the formation of a violet by-product which appears to be of interest as a self color.

A "Suggestion for Experimental Change in Process" form has been filed advocating the use of sodium sulfite in place of sodium bisulfite and sodium hydroxide

Patent Situation:

No change.

Experimental Results:

The experimental work undertaken arose out of trouble encountered in the plant production of Charge 129 of DuPont Anthraquinone Blue 3G. After heating for 15 hours according to the process, only about 50% of the charge had been converted as ascertained by the filtration test which filters off the insoluble, unconverted DuPont Anthraquinone Blue SKY. Further heating for another 15 hours was given the charge, but only slightly higher conversion was obtained.

On checking the temperature of the charge with a maximum thermometer, it was found that the "clock" was 13°C. too low. This seemed to be the explanation of the poor conversion and the temperature was raised to 98-100°C. and the charge boiled for another 15 hours. After this period, the filtration test was run again and it was found that conversion was still not complete being about 75-80% of what it should be. It was decided to check the pH of the charge.

pH Studies of the Conversion of DuPont Anthraquinone Blue SKY to DuPont Anthraquinone Blue 3G

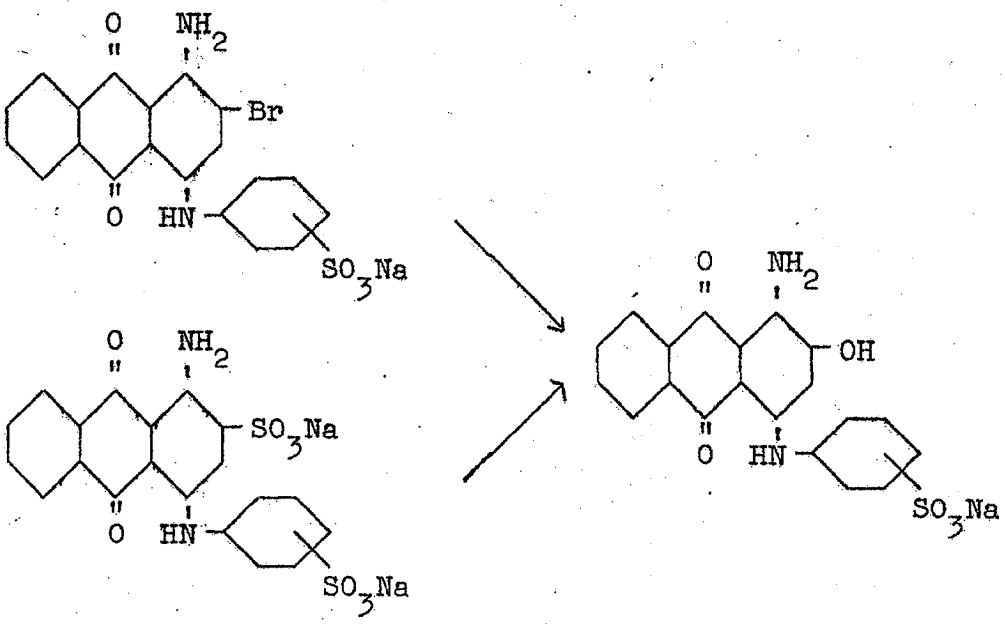
The pH on Charge 129 was taken and found to be 11.5. The process calls for a faint pink color on phenol-phthalein paper. Since this paper has a range of pH 8.6-9.8, it was suspected that the pH of 11.5 might be too high for optimum conversion of Blue SKY to

Blue 3G. A sample of this charge was taken into the laboratory, the pH was adjusted to pH 10 with sodium bisulfite and the sample heated for 15 hours. The filtration test showed 100% conversion. This experiment strongly indicated that more careful specifications of pH might be necessary for the conversion of Blue SKY to Blue 3G.

The process as now being run under standing orders differs from the older processes in being run in a much larger volume. This allows a little more leeway in adjustment of pH since it was later shown that the smaller the volume, the more important was the proper adjustment of pH. As adjusted in the plant to a faint pink color to phenol-phthalein; inaccurate results might prevail easily since the blue color of the Blue SKY solution masked the faint pink of the phenol-phthalein alkaline reaction. Further laboratory experiments (R. C. Seyler) showed that in the volume used in the plant at present, a pH as low as 7.3 could be used to satisfactorily convert Blue SKY to Blue 3G.

Moreover, it was found that there was a definite tendency for the more alkaline conversions to be somewhat redder and duller than those converted at a lower pH. There is a logical explanation for this fact.

It is known that the 2-bromo atom in 1-amino-2-bromo-4-aryl-amino-anthraquinone can be replaced by OH by treatment with alkali under various conditions. Similarly, a 2-sulfonic acid group can also be replaced according to the following reaction -



The 2-hydroxy compound is very violet and dull. A very dull red-violet was isolated from batch 129 which was probably formed

by the long extended heating of the Blue SKY under very alkaline conditions. This shows that high pH is also bad because of dull by-products which are formed in the reaction as well as preventing the conversion to Blue 3G.

Blue 3G Operation in Plant with Controlled pH

Following the attempted conversion of batch 129 to Blue 3G and the establishment of pH controls on the later batches, very satisfactory results were obtained. Five batches have been run to date, namely batches 130-134 at a pH varying between 8.3 and 9.6. All came out green and bright. The overall efficiency for these five batches was 112.6% of process.

In all of the above batches, the sodium sulfite was prepared by adding sodium bisulfite to a solution of NaOH. This is easily controlled by an experienced operator and with the aid of the laboratory and a pH meter. However, such careful control is difficult at night and if sodium sulfite could be used, no adjustment would usually be necessary. The pH of sodium sulfite in water is 9.2 which is ideal for the conversion of Blue SKY to Blue 3G. Since all batches of Blue SKY should be washed somewhere near the neutral point with brine, no adjustment is necessary. Now and then, however, a batch of Blue SKY is obtained which has not been washed entirely acid free. Such acidity reduces the pH of the conversion and when an acid batch is used, the pH must be checked. The use of sodium sulfite elimina tes the necessity of such controls (except in the special instance cited) since it automatically establishes the correct pH. It has another slight advantage in that it is cheaper than sodium bisulfite. It enables the color to be run on night shift without laboratory controls.

A "Suggestion for Experimental Change in Process" has been filed and if allowed, we will operate several charges using sodium sulfite. We expect to incorporate this change in a new Dye Works process for DuPont Anthraquinone Blue 3G to be written shortly.

Conversion of Blue SKY to Blue 3G in Small Volume

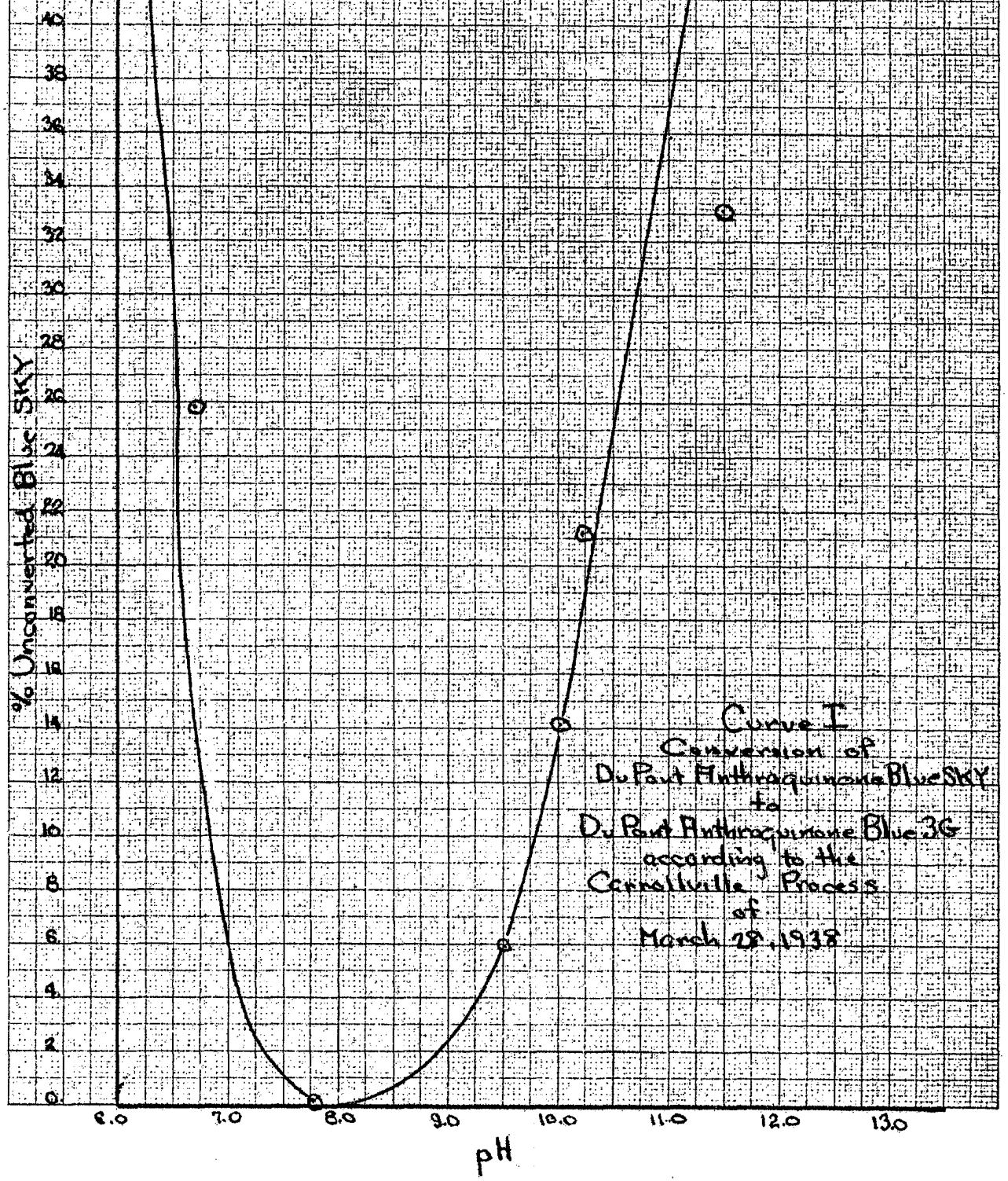
JLNB-4266, pages 43-53.

The Carrollville process of March 23, 1938 for DuPont Anthraquinone Blue 3G used a volume about half of that used at present. Such a process has the advantage of reducing costs through the possibility of running double charges in the same equipment now used. A series of experiments was run using the volumes of the old Carrollville process and checking the pH of the solutions used.

Experiments were run using sodium sulfite and sodium sulfite formed from sodium bisulfite and sodium hydroxide.

In the case of the conversions in the smaller volumes, it was found that the pH range over which conversions were complete was much narrower than in the case of the larger volumes. It appears that a range of about pH 8-9 gives complete conversion whereas the pH range in the case of the larger volume is longer from about 7.3 to 11.0 although we have limited it to about 9-10.

From curve one, it can be seen that acid conditions below pH 7 almost prevent the reaction entirely while alkaline conditions above pH 9.3 appear to be detrimental to the reaction too. While it is true that this short volume was successfully operated at Carrollville, additions of water to increase the volume so the reaction would go to completion were made at various times which showed that even under the proper conditions, incomplete conversions sometimes took place. For this reason, we are not recommending a return to the volumes of the Carrollville process. While the greater number of experiments performed under various pH values did lie on the parabolic curve shown, a few erratic results were obtained which confirmed our decision not to use the smaller volumes. It appears likely that under very carefully controlled conditions this short volume could be successfully used but it will take additional work to determine the various factors involved and the present importance of the color does not merit it. JLNB-4266, pages 40-55.



Effect of Acid-Containing Blue SKY on Conversion to 3G

Although an effort is made to wash all Blue SKY with brine until a neutral or slightly alkaline cake is obtained, a charge is now and then received which has an acid reaction. If such a charge is used for conversion to 3G and sodium sulfite is used for the conversion, the pH must be adjusted to 9.0-10.0 with additional sodium hydroxide.

Relation of Temperature to Conversion of Blue SKY to Blue 3G

The specified temperature for this conversion is 98-100°C. Lower temperatures result in incomplete conversion in the specified time of 15 hours and are likely to result in the formation of undesirable by-products. In plant operation, care should be taken to maintain the temperature and check all "clocks" and thermometers.

Effect of the Use of Inferior Sodium Bisulfite

While sodium bisulfite specifications call for a product 99% or better, products as low as 75% compound have been employed in plant practice. If better products are not available, such material may be used if it is first checked in the laboratory on a conversion. Its use, however, is not recommended.

Summary of Recommended Process for
DuPont Anthraquinone Blue 3G

Charge into an enamelled kettle 22,000 pounds of water followed by 605 pounds (100%) of sodium sulfite. When dissolved, add 350 pounds (100%) DuPont Anthraquinone Blue SKY crude press cake and suspend. (If the laboratory has reported the press cake "acid", a sample of the solution in the kettle should be sent to the laboratory for a pH determination which should be adjusted to pH 8-10 by additions of 30% sodium hydroxide or sodium bisulfite.)

Check the volume of the suspension in the kettle and heat the charge to 99-102°C. as rapidly as possible. Maintain a temperature of 99-102°C. for 15 hours adjusting the volume by addition of water as necessary in order to maintain the dilution at the original level. At the end of 15 hours, remove a one pint sample from the charge and send to the area laboratory for completeness of conversion and O.K. to filter.

When the charge is O.K.'d by the laboratory, add 70 pounds of Filter-Cel and cool to 60°C. over 1-1/2 - 2 hours. Filter at 60°C. through the sludge press collecting the filtrate. Wash down the kettle with 150-200 pounds of water and filter.

The temperature of the filtrate is adjusted to 50°C. and 3000 pounds salt are added over a two-hour period.

Agitate for 15-30 minutes and check specific gravity which should be 1.10-1.11.

Filter, suck dry and wash with 9000 pounds of 13% brine. Suck dry and dry at 100-110°C. (For details of tests and procedure see Dye Works process for the manufacture of DuPont Anthraquinone Blue 3G)

Goal Yield on Conversion of Blue SKY to Blue 3G

Upon the completion of the work of the conversion of DuPont Anthraquinone Blue SKY to Blue 3G, a series of experiments were run using sodium sulfite or a mixture of sodium bisulfite and sodium hydroxide adjusted to the proper pH for the purpose of setting up a "goal yield" (JLNB-4266, pages 49, 50, 53, 54, 66 - Ponsol Laboratory Notebook 491, page 81)

The following table shows the experiments used in arriving at this goal yield. An average of the six experiments was used for this yield figure.

Table 1

Conversion of DuPont Anthraquinone Blue SKY to DuPont Anthraquinone Blue 3G

JLNB Exp. No.	Grams Crude SKY	Grams Crude 3G	Dyetest	Grams Type 3G (Crude Converted)	Factor from Crude SKY	Efficiency over 3G Process
4266-66	117	121	55/100, sli. green & bri.	220	1.88	133.5
4266-54	35	39	55/100, sli. red	70.9	2.02	143.5
4266-50	42.6	38	55/100, sli. bright	69.0	1.62	115.0
4266-53	35.0	31	57/100, bri, sli. green	54.4	1.55	110.0
4266-49	42.6	39	55/100, sli. bright	70.9	1.66	118.0
Ponsol Lab. 491-81	25.0	24.0	55/100, tr. green, tr. bri.	43.7	1.75	124.0

Goal Yield:

1.750 - which compares with 1.408 of the Carrollville process for DuPont Anthraquinone Blue 3G dated March 23, 1938 and which will also be the yield of the new process just written until such time as the new process will have been operated long enough to set up a new standard.

The goal yield of 1.750 gives an efficiency of 124.4% of process. The first five batches of this color run in the plant using sodium bisulfite and sodium hydroxide under controlled pH gave an efficiency of 112.6%. In accordance with plant practice, if these high efficiencies are maintained over a longer period of time, the standard will be raised.

Bibliography

1 - Plant Process A - Color 3181 - DuPont Anthraquinone Blue 3G Meuly - Lee

2 - Carrollville Plant Process for DuPont Anthraquinone Blue 3G March 23, 1938

3 - Patent Search on above process. Case 289-A (Carrollville)

4 - Standing orders (plant) - January 7, 1944.

5 - U.S. 1,131,516 - Anilin Fabrikation - March 9, 1915.

6 - D.R.P. 288,878 - Bayer - May 2, 1914

7 - D.R.P. 163,647 - Bayer - August 10, 1912.

8 - The following are of lesser importance but somewhat related.

B.P. 7,861 (15), 10,378 (14)
D.R.P. 280,646
S.P. 70,157, 71,654, 71,655

No corresponding I.C.I. literature has been found.

Submitted
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2-23-44

Typed
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