AZOIC DYES AND INTERMEDIATES
FROM PHLOROGLUCINOL
DERIVATIVES

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James William Watters
B. S. in Chemistry, Howard College, 1930
M. S. in Engineering, University
of Cincinnati, 1944

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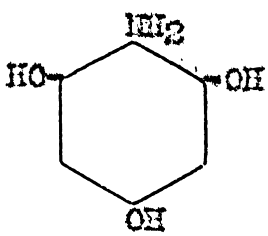
CONTENTS

INTRODUCTION

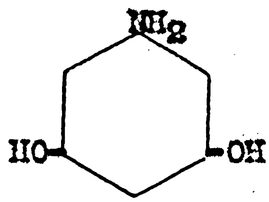
The present work was undertaken as one part of the research project established in the Applied Science Department by the Edwal Laboratories, to investigate the nature of dyes, pigments, and secondary intermediates which can be prepared from phloroglucinol and related compounds obtained from trinitro toluene by processes of reduction and hydrolysis, with or without demethylation.

The phase of the overall project to be discussed here was concerned only with compounds which were derived ultimately from phloroglucinol. This compound and its ethers and other simple derivatives are highly reactive, however; they undergo chemical transformations with such ease that any limitations due to narrowing the field of work are more apparent than real. Only a fraction of the numerous possibilities was explored.

While phloroglucinol was the common starting material in all the synthetic work, one group of the intermediates prepared may be looked upon as derived from amino phloroglucinol (not itself prepared) and the other as derived from 5-amino resorcinol, or phloramine. These compounds have the following structural formulas:



Amino Phloroglucinol

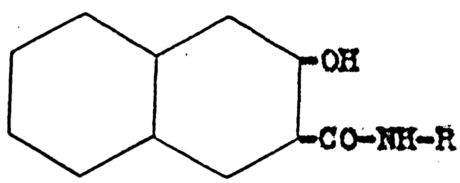


Phloramine
(5-Amino Resorcinol)

Of particular interest, in prospect, were 2,4,6-trimethoxy aniline, the trimethyl ether of amino phloroglucinol, and its homologs triethoxy aniline, tributoxy aniline, and so on. Trimethoxy aniline was prepared as an index of the properties of this series of amines.

Trimethoxy aniline appeared to have some possibilities as an amine base for preparing azoic acid wool colors, pigments, and ice colors for cotton and staple fiber rayon; although anisidines as a class are not particularly good for these uses, ortho anisidine is used to some extent as an ice color base. Trimethoxy aniline was considerably more interesting, however, as raw material for preparation of two of its condensation products which could be used as coupling components for ice colors and azoic pigments.

One of these products was the trimethoxy anilide of beta oxy naphthoic acid,* or BON. The arylides of this acid are known commercially as Naphthol AS, Naphthol AS-D, etc. They have the general formula



in which R represents an aryl group such as phenyl or

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* More correctly, 2,3-hydroxy naphthoic acid

naphthyl, which may bear substituents. Coupling occurs at the alpha position ortho to the hydroxyl group.

These arylides are the most widely used ice-color coupling components. Perhaps the chief explanation of this fact is that they have considerable affinity for cotton and staple fiber rayon and tend to dye the fabric in their own right, like direct cotton dyes, even before the final formation of the dye proper. Dyes from the BON arylides are often remarkably fast to light and wet treatments, and their shades are usually bright and attractive. Moreover, although the R group of the formula above ought to be far enough from the azo group of the final dye to have little effect on the color, this is not actually the case. A considerable range of variation is possible through changing the R group or its substituents.

The other condensation product was the acetoacetyl derivative of trimethoxy aniline. Acetoacetarylides are used as coupling components for azoic pigments. They have the formula

$$H_3C-CO-CH_2-CO-NH-R$$

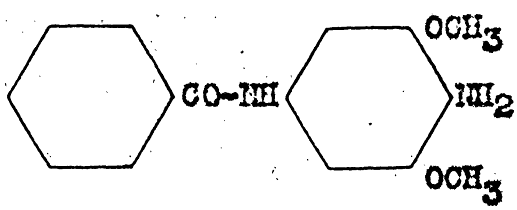
in which R has the same significance as in the formula for BON arylides. Coupling takes place at the methylene group between the two carbonyls.

In the past, the best results as regards lightfastness have been obtained with arylides prepared from ortho- or para-substituted arylamines - such as ortho toluidine, ortho anisidine, 2,5-dimethoxy aniline, 2-methyl 4-chloro aniline, etc. This favorable effect of ortho and para substituents can be explained, if somewhat primitively, on the basis of the commonly accepted view, supported by a considerable body of evidence (1-10), that fading on exposure to sunlight is caused in most cases, and particularly where azo compounds and arylamides are involved, by air oxidation catalyzed by the light. Blocking of the ortho and para positions by substituent groups would lessen the tendency to form ortho and para quinones, and hence would decrease the ease of oxidation. The effect of ortho substitution is somewhat greater than that of para substitution, perhaps because a group in the ortho position hinders sterically the entrance of oxygen (or the abstraction of electrons) at the aryl-nitrogen bond. Since in trimethoxy aniline the para position and both positions ortho to the amino group are occupied, it seemed reasonable to expect good lightfastness from its derivatives.

Another conception, that of electronegativity, also leads to the assumption that trimethoxy anilides would exhibit favorable properties. The electronegativity of a chemical group is proportional to, and in fact is measured by, the tenacity with which it holds the bonding electrons between it and the atoms or groups to which it is attached. A number of workers, notably Tiffeneau (11-13), Kharasch (14, 15), Bachmann (15-20), and their co-workers, have measured relative electronegativities of a large number of groups, including substituted phenyl groups, through decompositions or rearrangements of compounds in which two groups were present and could be compared. Results of the various investigators are in fair agreement; in all cases, methoxy-substituted phenyl groups have proved to be highly electronegative. Moreover, empirical examination of a large number of substituted acetoacetanilides, as coupling components in azoic pigments,* indicated that lightfastness was roughly proportional to the electronegativity of the aryl groups. From correlation of these facts, it appeared that the trimethoxy phenyl radical would be highly electronegative and that for this additional reason the condensation products of trimethoxy aniline would have desirable properties.

Like trimethoxy aniline, the similar phloramine ether, 3,5-dimethoxy aniline, was chiefly interesting as raw material for preparation of more complex intermediates. The two intermediates of most immediate interest were

2,6-dimethoxy 4-benzoylamino aniline



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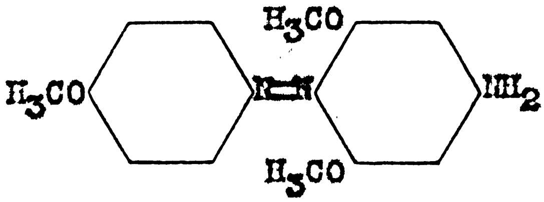
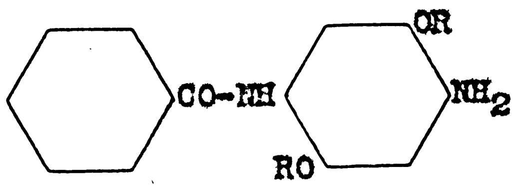
* Unpublished work of W. B. Reynolds

and 2,6,4'-trimethoxy 4-amino azobenzene



The first of these would be prepared by coupling diazotized sulfanilic acid with 3,5-dimethoxy aniline, benzoylating the product, and then reducing the benzoylated azo compound. The second would be prepared by coupling diazotized 4-anisidine with 3,5-dimethoxy aniline.

In prospect, these two intermediates were of interest chiefly as ice-color bases, although they might also have some application to the preparation of azoic pigments, acid wool colors, or direct cotton dyes. The dimethoxy benzoylamino aniline resembles a group of ice-color bases, widely used commercially, which have the general formula



in which the R represents an alkyl group (21, 22). These amines give blue colors of varying depth with a wide variety of coupling components. The similar compound to be prepared with the alkoxy groups in the 2,6-positions instead of the 2,5- was expected to give at least as great a depth of color. Such a blue base would be a valuable article of commerce, especially if it proved to give dyes of good fastness.

Likewise, the trimethoxy amino azobenzene, by analogy with a number of dyes in which methoxy groups are ortho to azo groups, was expected to give blue or dark crimson shades.

Besides having satisfactory fastness and a desirable shade, a good ice color must be bright and clear, free from the dullness which makes many otherwise excellent dyes unattractive. Methoxy-substituted ice-color intermediates in general rank high on this score, another fact which augured well for the intermediates to be prepared.

EXPERIMENTAL PART

The greater part of the experimental work was the synthesis of the necessary compounds. Trimethoxy and dimethoxy aniline were of course the key compounds to be prepared.

Trimethoxy aniline was prepared through amination of trimethoxy benzene, and one method tried for preparation of dimethoxy aniline was ammonolysis of dimethoxy phenol. Hence supplies of these methyl ethers of phloroglucinol were needed, and a method of preparing them was worked out.

The synthetic method finally adopted for 3,5-dimethoxy aniline involved (1) preparation of phloramine by ammonolysis of phloroglucinol, (2) acetylation of phloramine to 5-acetylamino resorcinol, (3) selective methylation of the hydroxyl groups of acetylamino resorcinol, and (4) hydrolysis of the dimethoxy acetylamino compound so obtained to get the dimethoxy aniline. A number of the compounds obtained along the way in this rather complicated synthesis were new, and had to be analyzed and characterized. This is true also of trimethoxy aniline and all its derivatives.

After preparation of the more complex intermediates discussed above from the trimethoxy and dimethoxy anilines, they were evaluated by preparing from them pigments and ice colors, which were tested for fastness to light.

Methylation of Phloroglucinol

A fairly satisfactory method for preparation of trimethoxy benzene has been known for some time (23), but the known methods for dimethoxy phenol (24, 25) and methoxy resorcinol (26) gave poor yields or were inconvenient.

Bases of the Present Procedure - The methylation procedure which was evolved in the course of some two or three dozen preparations of trimethoxy benzene and dimethoxy phenol is based on four main considerations:

(1) Phloroglucinol methyl ethers, unlike those of other phenols, cannot be formed by reacting the phenol with aqueous alkali and methyl sulfate. Instead, these reagents lead to attachment of methyl groups to the six-membered carbon ring (27). If ethers are to be obtained, an acid methylating agent is essential as long as unmethylated phloroglucinol is present.

(2) Intermolecular condensation occurs quite readily with phloroglucinol, so that high temperatures and highly concentrated reagents, whether acid or alkaline, must be

avoided.

(3) Since phloroglucinol has three functional groups, the methylation occurs in steps. A mixture of mono-, di-, and tri-methyl ethers is always obtained, so that tedious separations must be carried out. The proportions of the three ethers obtained may be varied, within limits, by varying the quantities of reagents used and the reaction time.

(4) Separation of the three products is possible because of solubility differences. The trimethyl ether, a solid at room temperature, is insoluble in aqueous alkali, in which both the other compounds are soluble. In acid or neutral aqueous media, the monomethyl ether is highly soluble, the dimethyl ether only slightly so. The dimethyl ether is readily extractible from such a medium with benzene, which removes only a negligible amount of the monomethyl ether. Finally, the monomethyl ether can be extracted from its aqueous solution with diethyl ether.

<u>Preparation and Separation of Crude Phloroglucinol Ethers</u> - One methylation, on a 4.5-molar scale, was carried through the following steps:

(1) Seven hundred twenty-one grams (4.5 moles) of phloroglucinol dihydrate were refluxed with 1701 gms of methyl sulfate (3 mole parts) in 4.5 liters of solvent-grade methanol for about 16 hours. The reagents were contained in a 12-liter round-bottom flask heated in a water bath by a steam coil and fitted with two 2-foot reflux condensers,

one atop the other. The bottom condenser was straight-walled, about three-fourths inch in inside diameter; the upper condenser was a bulb condenser of somewhat smaller minimum inside diameter. An efficient reflux system of large capacity, such as the one described, is needed because large quantities of dimethyl ether are formed in the first part of the reflux period, and the dimethyl ether vapors entrain considerable methanol.

(2) The methanol solution was allowed to cool. The original 12-liter flask was fitted with a vapor-tight stirrer, passing through the same rubber stopper as the lower reflux condenser, the condensers being left in place. Then 3150 ml of 10N NaOH (7 mole parts) were added in small portions through the condensers, with stirring, followed by 1350 ml of water which were added in such a way as to wash down the sides of the condensers. Then refluxing was resumed for about 16 hours; during this reflux period stirring was necessary to prevent bumping.

(3) The reaction mixture was allowed to cool, then filtered. From the residue, a mixture of trimethoxy benzene and sodium sulfate, the sodium sulfate was removed by stirring with five liters of water warmed to 40-45°C, and refiltering. One hundred seventy grams of crude trimethoxy benzene (22.5%) were obtained. The crude product was grey in color and melted at about 50°C.

(4) The filtrate from step (3) was concentrated in

vacuo till crystals of trimethoxy benzene began to appear in the distillate. The aqueous concentrate on cooling yielded an additional 26.5 gms (3.5%) of crude trimethoxy benzene, which were filtered off. From the methanolic distillate an additional 3.8 gms (0.5%) of trimethoxy benzene were recovered by addition of 2.5 times its volume of 25% W/V aqueous NaCl. The trimethoxy benzene was precipitated and filtered off.

(5) The filtered aqueous concentrate from step (4) was acidified with 375 ml of concentrated HCl. The total volume was then about 4500 ml, which was divided into three approximately equal parts. The three parts were then extracted successively with five 450-ml portions of solvent-grade benzene. The benzene extract was filtered through cotton, after which the benzene was removed in vacuo, yielding 350 gms (50.4%) of crude dimethoxy phenol. This product was an oily viscous amber liquid, with a strong phenolic odor.

In the preparation described, methoxy resorcinol was not isolated. However, if isolation had been desired it could have been carried out as follows:

(6) The benzene-extracted aqueous concentrate is finally extracted with five portions of diethyl ether, each about 30% of the volume of the aqueous solution. (Note that diethyl ether extracts the dimethoxy phenol as well as the methoxy resorcinol, unless the former is first extracted with benzene.) Evaporation of the ether yields not more than 5-10%

of the theoretical amount of methoxy resorcinol. The yield was 1% in one methylation similar to that described. The crude methoxy resorcinol is an amber-colored liquid, but crystallizes on standing.

If the refluxing of step (2) is omitted, the yields are different. In one such case, the yields were 10.4% of trimethoxy benzene, 25.7% of dimethoxy phenol, and 57.3% of methoxy resorcinol.

Purification and Properties of the Ethers - 1,3,5-Trimethoxy benzene can be purified by steam distillation, followed by crystallization from 4 to 6 ml per gram of low-boiling petroleum ether. It is a compact white crystalline solid (prisms from alcohol, needles from petroleum ether) melting at 54-55°C and boiling without decomposition at 255.5°C (corrected) at atmospheric pressure. It has a characteristic pleasant odor and as indicated is volatile in steam. Insoluble in water and cold petroleum ether, it is fairly soluble in other common solvents.

3,5-Dimethoxy phenol is purified by vacuum distillation, followed by crystallization from a mixture of benzene and low-boiling petroleum ether. Large transparent crystals (platelets) can be obtained. The melting point is 44°C (corrected), and the boiling range at 17 mm pressure is 172-175°C. Dimethoxy phenol is similar to unsubstituted phenol in appearance, odor, and behavior with solvents, but lacks its irritating effect on human skin.

5-Methoxy resorcinol is difficult and inconvenient to purify. It cannot be distilled even at fairly low pressures without considerable loss. When distillation is attempted at 4-6 mm, intermolecular condensation occurs, resulting in simultaneous resinification and distillation of water along with some methoxy resorcinol. The distillation rate and boiling point do not become constant (the latter ranged from 168 to 178°C in one instance). The distillate is a mixture of hydrated and anhydrous methoxy resorcinol.

Pure samples of methoxy resorcinol can be obtained, however, by crystallization from benzene. The crude product is first triturated once or twice with a convenient volume of cold benzene, to remove the dimethoxy phenol which is always present. Then it is crystallized from 40 to 50 ml per gram of benzene, the hot benzene solution being dried by means of a side-arm reflux. Benzene dissolves about 3.3 gms of anhydrous methoxy resorcinol per 100 ml at the boil.

Compact white crystals (prisms) can be obtained by two such crystallizations from benzene. The melting point is 85°C (corrected). A hydrated form melting at 36-38°C is reported in the literature (26). Samples of the anhydrous compound whish are not carefully purified may melt as low as 60°C.

Methoxy resorcinol is extremely soluble in hydroxylic solvents, giving syrupy solutions when concentrated. It is also quite soluble in diethyl ether and acetone. It is insoluble in petroleum ether and in cold benzene, chloroform, and carbon tetrachloride.

Preparation and Properties of 2,4,6-Trimethoxy Aniline

The method of preparation depends on the coupling of trimethoxy benzene in dilute acetic acid with diazotized sulfanilic acid, followed by reduction of the resulting azo compound with sodium hyposulfite, $Na_2S_2O_4$. Coupling to trimethoxy benzene was first described by K. H. Meyer and Lenhardt (28). A preparation carried out on a half-molar scale is described:

The diazo compound was prepared from 86.5 gms of CP anhydrous sulfanilic acid (0.5 mole). The dry sulfanilic acid was mixed with a spatula by hand in a 600-ml beaker with 35 gms (about 0.5 mole) of sodium nitrite. One hundred fifty grams of crushed ice and 50 ml of water were added to the mixture, with stirring by hand. Finally a cold mixture of 22 ml of concentrated sulfuric acid (0.75 equivalent), 50 gms of crushed ice, and 50 ml of water was added, and stirring was continued for 10 or 15 minutes. Excess nitrous acid was destroyed by adding a little dissolved sulfamic acid. The final diazo suspension was a thin slurry.

This was added portionwise to a stirred and externally cooled solution of 88.2 gms of crude trimethoxy benzene (0.525 mole) in 400 ml of glacial acetic acid containing 123 gms of anhydrous sodium acetate (1.5 moles). The trimethoxy benzene solution was in a 1500-ml beaker. The sodium acetate did not all dissolve before addition of the diazo compound; the cooling bath froze the acetic acid to a mush which melted as the diazo mixture was added. Two hundred milliliters additional glacial acetic acid were used to wash in the last portions of the diazo slurry and to wash down the sides of the container. Stirring was continued for 36 hours, the temperature of the reaction mixture being kept below 5°C for the first 12 hours.*

The azo sulfonic acid formed in the coupling reaction was a bright red crystalline solid. It was filtered off with suction, washed with 75 ml of glacial acetic acid, and dried in an air draft until free from the odor of acetic acid. The product weighed 236.8 gms, or about 135% of theory for 2,4,6-trimethoxy azobenzene 4'-sulfonic acid. Ash and total sulfur determinations indicated contamination with sodium sulfate and some sodium acetate, with practically the theoretical yield of azo compound.

The reduction of the azo compound was carried out in a 2-liter 3-neck round-bottom flask fitted with reflux, vapor-tight stirrer, and powder funnel. A solution was prepared of 220 gms of the azo compound (assumed to be 0.48 mole) and 100 gms of NaOH (2.5 moles) in about 750 ml of water. In the round-bottom flask, 200 ml of water were stirred and

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* Diazotized sulfanilic acid appears to be less stable in acetic acid solution than in water, and coupling is accompanied by considerable evolution of heat. Hence the use of the external cooling bath. The diazonium sulfate is preferred to the chloride as being more stable.

heated on a steam bath. To the hot water were added portionwise 225 gms of sodium hyposulfite (1 mole of $Na_2S_2O_4$ by iodine titration) and the azo solution, alternating additions in such a way that the mixture was kept just decolorized. Finally, the reaction mixture was heated and stirred for 2 hours and allowed to cool overnight. There were then present about 100 gms of crystalline solid and about a liter of liquid, including some oily droplets.

The liquid was decanted from the solid crystals, which were then dissolved in about 400 ml of water. The two liquids were extracted successively with 5 100-ml portions of benzene. Removal of the benzene in vacuo gave 61 gms of crude product. This was fractionated at 12 mm in a nitrogen atmosphere (maintained by bubbling a capillary stream of nitrogen through the boiling liquid). The main fraction, an oil, boiled at 159 to 160.5°C (uncorrected) and weighed 50.5 gms (57.3%).

A portion was redistilled in vacuo, again in a nitrogen atmosphere. Twenty grams of the redistilled material were dissolved in 20 ml of CP benzene, filtered, and stirred, with external cooling, during dropwise addition of 100 ml of low-boiling petroleum ether. White crystals appeared; they were suction-filtered, washed with a mixture of 8 ml of benzene and 40 ml of petroleum ether, and dried, first by aspirating air through the filter and then in vacuo over calcium chloride.

The dried crystals weighed 15.8 gms (79% recovery).

When viewed under a low-power microscope (15x) they were seen to be minute clusters of short branched cylindrical rods. They had a pale pink cast, scarcely noticeable, which appeared while they were being air-dried. The melting point was 33°C (corrected). Refractive index at the melting point was 1.5559, at 35°C 1.5555. Trimethoxy aniline is soluble in all the common organic solvents except petroleum ether, and slightly soluble in water.

Analytical Data -

	Calculated for $C_9H_{13}NO_3$	Found
% Carbon	59.00	59.03 (58.82)
% Hydrogen	7.15	7.09 (6.94)
% Nitrogen	7.64	7.76 (7.77)

Preparation of 3,5-Dimethoxy Aniline

3,5-Dimethoxy aniline is mentioned in the literature (29), having been prepared by Seka and Fuchs from 3,5-dimethoxy benzoyl amide by a Hofmann rearrangement. These workers also describe the benzoyl derivative of the amine.

As already indicated, the preferred synthetic method given here depends upon successive application of processes of acetylation, methylation, and hydrolysis to phloramine, which is prepared from phloroglucinol by ammonolysis.

Preparation and Properties of Phloramine - Phloramine was first described by Hlasiwetz (30), who prepared it by allowing a mixture of 10 gms of phloroglucinol and 50 ml of ammonia to stand, apparently in an open beaker, "for a few hours." Pollak (31) was unable to prepare phloramine by Hlasiwetz' procedure, but he did get a good yield of phloramine by sealing the reagents in a hydrogen-filled glass tube and allowing them to stand for 2 or 3 days.

When preparation of phloramine for the present work was attempted, it soon became apparent that Pollak's elaborate precautions to prevent oxidation of the product are unnecessary. The large excess of ammonia used by both investigators appears to be not only unnecessary but undesirable. Several batches of phloramine were prepared merely by stirring an aqueous suspension of phloroglucinol dihydrate with a 10% excess of ammonia for 1 to 2 hours.

In the experiment which gave the best yield, a mixture of 197.6 gms of phloroglucinol dihydrate (1.22 moles) with 88 ml of concentrated aqueous ammonia (SG 0.9; about 1.34 moles) and 125 ml of distilled water was stirred at room temperature for one hour, in a 1-liter Erlenmeyer fitted with a vapor-tight stirrer and an inward-outward Bunsen valve to reduce contact with the air. Then the reaction mixture was refrigerated for 5 hours and suction-filtered. The residue was washed with 50 ml of ice water, dried in vacuo over sulfuric acid, and pulverized. The product was a pale silver-grey powder with a slight but definite odor of ammonia; it weighed 138.5 gms (90.5%).

When heated rapidly, freshly prepared phloramine decomposes sharply, with effervescence, at some temperature between 135 and 155°C, the exact temperature depending on the rate of heating. When held at 100-110°C for any length of time, phloramine slowly resinifies. It darkens and decomposes gradually when exposed to light and air, especially in aqueous solution. It is fairly soluble in water, even at 0°C, and in other hydroxylic solvents, but not in ether or non-polar solvents generally. The solubility in water increases rapidly as the temperature rises.

Preparation and Properties of 5-Acetylamino Resorcinol - The problem of acetylating phloramine to get good yields of 5-acetylamino resorcinol was not satisfactorily solved. The phloramine appears to decompose during the course of the acetylation; the decomposition may be catalyzed by small amounts of impurities.

A good yield was obtained in one case, however, when 12.5 gms of freshly prepared phloramine (0.1 mole) were suspended in 25 ml of water and treated with 10.2 gms of acetic anhydride (0.1 mole) at room temperature. Reaction was immediate; heat was evolved and the finely powdered phloramine was replaced by a crystalline precipitate of somewhat larger particle size. This was separated and air-dried, the crude product weighing 13.5 gms (81%).

Other experiments with the same or slightly different procedures gave yields as low as 10%.

5-Acetylamino resorcinol can be purified by recrystallization from acetic acid or, preferably, from water (3 to 5 ml per gram). It is soluble in ethanol and methanol, slightly soluble in cold water and cold glacial acetic acid, insoluble in non-polar solvents. It is a colorless crystalline solid (needles) which melts at 223.5°C (corrected).

Analytical Data -

	Calculated for $C_8H_9NO_3$	Found
% Carbon	57.48	57.38 (57.31)
% Hydrogen	5.43	5.36 (5.28)
% Nitrogen	8.38	8.37 (8.58)

Preparation and Properties of Acetyl 3,5-Dimethoxy Anilide - Methylation of 5-acetylamino resorcinol with aqueous alkali and methyl sulfate was tried somewhat timidly, at first, as a test-tube experiment, since it was feared that methylation of the hydroxyl groups would be accompanied by hydrolysis of the acetyl group and simultaneous methylation of the unblocked amino group. However, the experiment was very successful.

One and sixty-seven hundredths grams of acetylamino resorcinol (0.01 mole) was dissolved in 4.4 ml of 10N NaOH (0.044 mole) and 2.5 ml of water, and shaken with 2.52 gms of methyl sulfate (0.02 mole). The test tube was cooled occasionally in tap water. Precipitation of the white solid acetyl dimethoxy anilide occurred almost immediately. This was separated and dried; the yield was 1.15 gms (59%).

Repetition with 0.31 mole of acetylamino resorcinol and proportionate amounts of the other reagents gave 21.0 gms of acetyl dimethoxy anilide (34.7%). This poor yield, as compared with that in the test-tube experiment, was probably due to poor temperature control of the reaction mixture.

Acetyl 3,5-dimethoxy anilide crystallizes as white needles from water, dilute ethanol, or xylene. It melts at 154.5°C (corrected) and is insoluble in most common solvents in the cold.

Analytical Data -

	Calculated for $C_{10}H_{13}NO_3$	Found
% Carbon	61.52	61.55 (61.74)
% Hydrogen	6.71	6.65 (6.77)
% Nitrogen	7.17	7.18 (6.91)

Hydrolysis of Acetyl 3,5-Dimethoxy Anilide - Twenty and eight-tenths grams of crystalline acetyl 3,5-dimethoxy anilide (0.107 mole) were refluxed for 4 hours with 60 ml of 10N NaOH (0.6 mole) in a mixture of 40 ml of water and 100 ml of methanol. Extraction of the cooled mixture with 4 100-ml portions of benzene gave 14.3 gms of crude dimethoxy aniline (79.4%).

Properties of 3,5-Dimethoxy Aniline - For purification, the crude dimethoxy aniline from the experiment just described was combined with other crude material containing diazotizable amine believed to be dimethoxy aniline. The total crude, weighing 30.3 gms, was fractionated at about 12 mm; the main fraction distilled at 158-159°C and weighed 18.0 gms. It was dissolved in 25 ml of benzene and filtered. The solution was stirred, with external cooling, during drop-wise addition of 150 ml of low-boiling petroleum ether. Clusters of small white needle-shaped crystals were precipitated. The purified material weighed 14 gms when dried.

Two grams were further purified by solution in acid and reprecipitation with sodium acetate, followed by another re-crystallization from benzene and petroleum ether. The purified amine is a fluffy white material melting at 53.3°C (corrected). Soka and Fuchs give 46°C. In behavior with solvents and ease of oxidation, dimethoxy aniline resembles unsubstituted aniline, but it lacks the pronounced odor of that compound.

Analytical Data -

	Calculated for $C_8H_{11}NO_2$	Found
% Carbon	62.72	62.85 (62.87)
% Hydrogen	7.24	7.29 (7.38)
% Nitrogen	9.15	9.28 (8.88)

Benzoyl 3,5-Dimethoxy Anilide - The benzoyl derivative of dimethoxy aniline was prepared chiefly because its melting point is given by Soka and Fuchs (29). A small quantity was made by a Schotten-Baumann reaction and recrystallized from a large volume of water. The melting point was 138°C (corrected). Soka and Fuchs give 139°C.

Analytical Data -

	Calculated for $C_{15}H_{15}NO_3$	Found
% Carbon	70.02	70.18 (69.75)
% Hydrogen	5.88	5.95 (5.89)
% Nitrogen	5.44	5.25 (5.22)

Ammonolysis of 3,5-Dimethoxy Phenol - Ammonolysis of dimethoxy phenol was the first method tried for preparation of dimethoxy aniline. In the first experiment carried out, a small amount of diazotizable amine was obtained by bubbling ammonia for 48 hours through a refluxing solution of dimethoxy phenol in xylene. The yield was so small as to be negligible, and this exact method of preparation was not pursued further.

In each of the other two ammonolysis experiments, 77.1 gms of dimethoxy phenol (0.5 mole) was autoclaved with aqueous ammonium sulfite prepared by bubbling sulfur dioxide into 200 ml of cold concentrated ammonia (SG 0.9) until the increase in weight was 50 gms. This is the well-known Bucherer method (32).

In the first of these experiments, heating was at 142 to 162°C for 17 hours. The autoclave was opened when leakage developed. A few drops of diazotizable amine were isolated.

In the final experiment, heating was at about 160°C (plus or minus 5°) for five days. When the autoclave was opened, most of the contents was charred, but two grams of material containing diazotizable amine were isolated by making the reaction mixture highly alkaline with sodium hydroxide and extracting with benzene. This product was fractionated in vacuo. The main fraction weighed about half a gram and was collected at 175-182°C and 12 mm. It solidified on standing at 0°C.

The acetyl derivative of this amine was prepared by the action of acetic anhydride in xylene on half the main fraction. Mixed melting points were taken of both the amine and the acetyl derivative with the amine and acetyl derivative obtained through methylation of 5-acetylamino resorcinol, and the compounds were found to be identical.

The autoclave experiments were discontinued partly because apparatus which would supply agitation under pressure was not available, and would have had to be built, and partly because the optimum temperature, concentrations, and reaction time for this reaction were not known, and would have had to be determined by trial and error.

<u>Condensation Products of 2,4,6-Trimethoxy Aniline</u>

<u>Acetyl 2,4,6-Trimethoxy Anilide</u> - The acetyl derivative was prepared for further characterization of trimethoxy aniline. A few drops of trimethoxy aniline were warmed in xylene with a 10% excess of acetic anhydride. The product appeared as white crystals (clusters of long needles) when

the solution cooled, and was purified by recrystallization from water (15 ml per gram). The melting point was 147.7°C (corrected).

Analytical Data -

	Calculated for $C_{11}H_{15}NO_4$	Found
% Carbon	58.65	58.67 (58.39)
% Hydrogen	6.71	6.76 (6.76)
% Nitrogen	6.22	6.22 (6.24)

Acetoacetyl 2,4,6-Trimethoxy Anilide - A solution of 13.3 gms of trimethoxy aniline (0.075 mole) in 40 ml of xylene was added dropwise to a refluxing solution of 13.0 gms of acetoacetic ester (0.1 mole) in 25 ml of xylene. The acetoacetic ester solution was in a 500-ml Claisen flask fitted with dropping funnel, thermometer, and downward water-cooled condenser. The trimethoxy aniline solution was added over a period of about 45 minutes, while the reaction mixture was heated just sufficiently to distill off the ethanol formed without loss of xylene. Heating was continued for fifteen minutes after all the trimethoxy aniline had been added.

Then the xylene solution was stirred by hand with a mixture of 10N HCl and 50 gms of crushed ice. The precipitated aceto-acetyl trimethoxy anilide was filtered off and purified by solution in caustic and reprecipitation with acid. The yield of purified product was 11.4 gms (57%).

A portion was further purified by several recrystallizations from water. The final product, fine pale amber needles, melted at 135.7°C (corrected).

Analytical Data -

	Calculated for $C_{15}H_{17}NO_5$	Found
% Carbon	58.41	58.43 (58.55)
% Hydrogen	6.41	6.27 (6.20)
% Nitrogen	5.24	5.26 (5.41)

2,3-Hydroxy Naphthoyl 2',4',6'-Trimethoxy Anilide - A mixture of 27.5 gms of BON (0.146 mole) and 25 gms of unpurified trimethoxy aniline (about 0.137 mole) in 200 ml of xylene was heated with stirring in a 500-ml round-bottom flask provided with a reflux, dropping funnel, and vapor-tight stirrer. When the temperature reached 70°C, heating was discontinued and 8.1 gms of phosphorus trichloride (5.2 ml; 0.059 mole) were added gradually through the dropping funnel. Then the reagents were refluxed until HCl ceased to be evolved, signalling completion of the reaction. Fifty milliliters of water and 15.9 gms of Na_2CO_3 (0.3 equivalent) were added to the reaction mixture, after which a downward condenser was connected and the xylene removed by steam distillation. Then the crude anilide was filtered off.

This was wet out with 50 ml of ethanol, stirred with 30 ml of 10N NaOH (0.3 mole), and dissolved in 400 ml of water. The basic solution was filtered and stirred during dropwise addition of a solution of 25.2 gms of $NaHCO_3$ (0.3 mole) in 300 ml of water. Reprecipitation of the anilide was completed by adding a few small lumps of dry ice. The purified product was separated and dried at 60°C. The yield was 38.2 gms (79%).

A portion was further purified by three recrystallizations from about 15 ml per gram of glacial acetic acid. After being dried in vacuo over sulfuric acid, the purified product, consisting of fine pale amber needles, melted at 221°C (corrected).

Analytical Data -

	Calculated for $C_{20}H_{19}NO_5$	Found
% Carbon	67.97	68.00 (67.94)
% Hydrogen	5.42	5.34 (5.32)
% Nitrogen	3.96	3.90 (4.21)

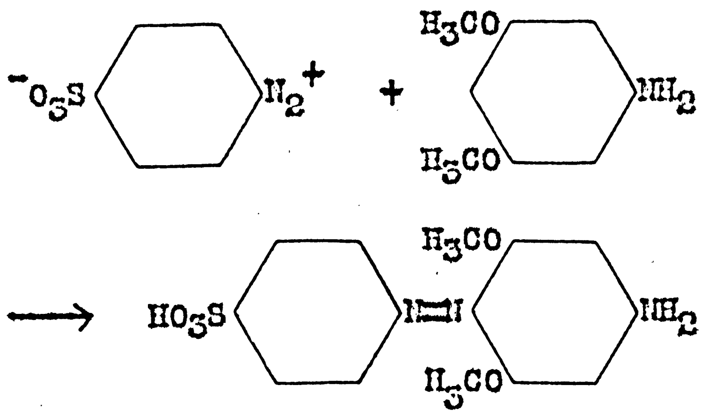
The procedure for preparation of the BON derivative of trimethoxy aniline has been given in some detail because it is the general method for preparation of BON arylides. Several arylides which were not obtainable commercially and which were wanted for comparison with the trimethoxy anilide were prepared in this way.

Complex Intermediates from 3,5-Dimethoxy Aniline

The structures ascribed to these products are based on the assumption that the respective diazo compounds couple with dimethoxy aniline at the para position to the amino group. Coupling with unsubstituted aniline is at the para position to the extent of over 90%.

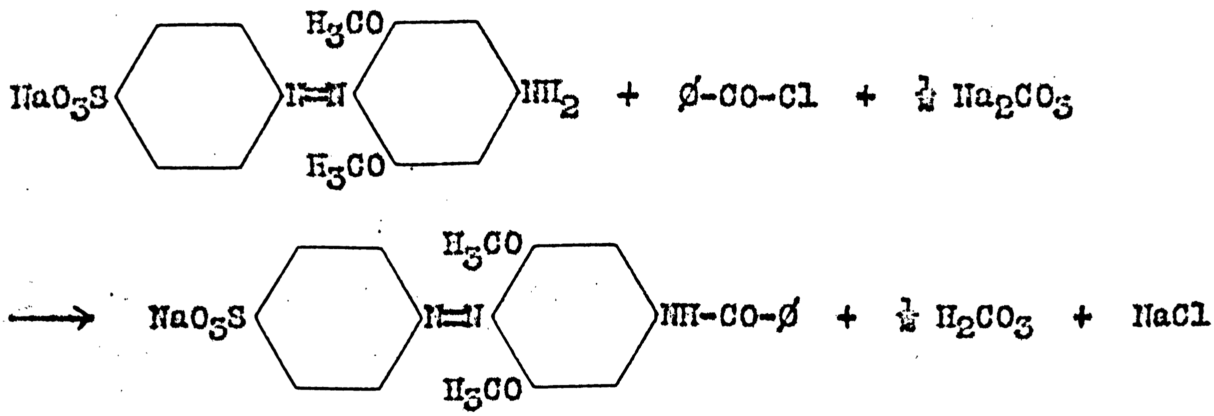
Preparation of 2,6-Dimethoxy 4-Benzoylamino Aniline - The following three steps were involved in this preparation:

(1) Three-hundredths mole of diazotized sulfanilic acid was prepared as described on page 14 and added portionwise, with stirring, to a slurry prepared by adding 33 ml of 4N sodium acetate (0.15 mole) to a solution of 5.0 gms of dimethoxy aniline (0.033 mole) in 50 ml of water and 16.5 ml of 2N HCl (0.033 mole). The reaction may be represented as follows:



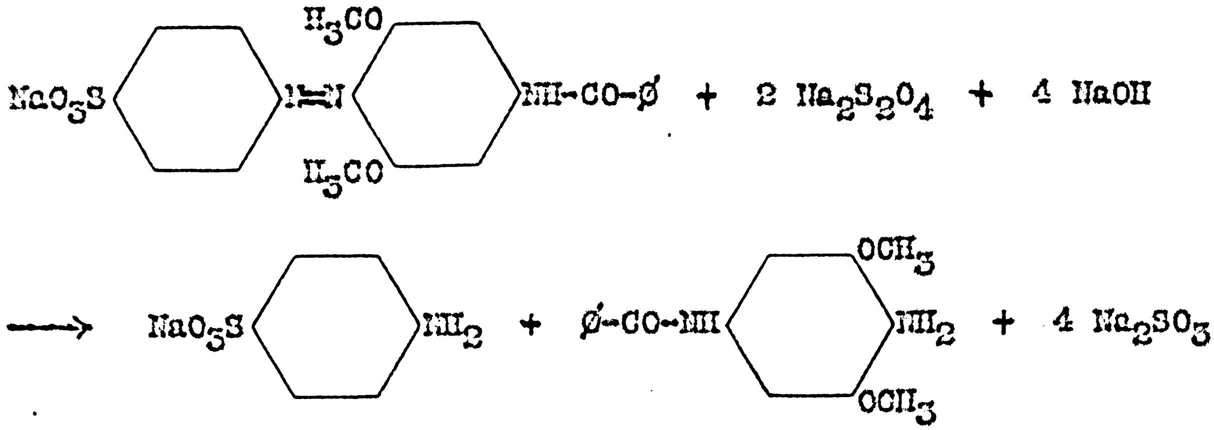
The product was filtered off, washed with 15% NaCl solution, and dried in vacuo over sulfuric acid.

(2) The azo amino sulfonic acid product was benzoylated by treating its sodium salt, in about 350 ml of sodium carbonate solution, with benzoyl chloride:



Successive additions of carbonate and benzoyl chloride (not weighed) were made, with vigorous agitation, until the mixture no longer contained diazotizable amine. The carbonate used was just enough to keep in solution the sulfonic acid and the benzoate formed by hydrolysis of unused benzoyl chloride. The final volume of the solution was about 400 ml; it was used as was for the final step.

(3) After addition of 17.6 gms of NaOH (0.44 mole), the solution was warmed to about 80°C. Then enough sodium hyposulfite was added in small portions, with stirring, to decolorize the hot mixture completely. The dimethoxy benzoylamino aniline precipitated as it formed. It is uncertain whether the hyposulfite is oxidized to sulfate or to sulfite, but if one assumes the latter an equation may be written as follows:



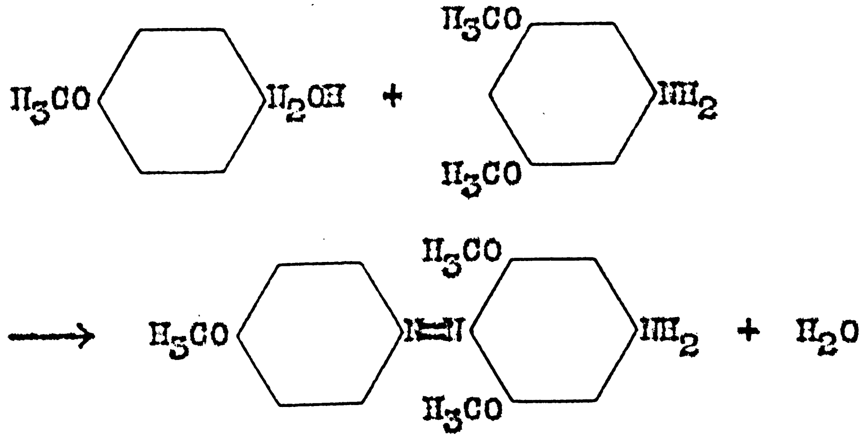
The product was purified by solution in hydrochloric acid and reprecipitation with sodium acetate. The overall yield was 5.6 gms (64%) of shiny light-grey crystals which softened at 174 and melted at 176°C (corrected).

One gram was further purified by two crystallizations from 25 ml of boiling benzene to which just enough ethanol (anhydrous) was added, dropwise, to bring about solution. In this way was obtained about half a gram of small pale amber needles which melted at 176.8°C (corrected).

Analytical Data -

	Calculated for $C_{15}H_{16}N_2O_3$	Found
% Carbon	66.16	66.12 (66.04)
% Hydrogen	5.92	5.74 (5.71)
% Nitrogen	10.29	10.23 (10.15)

Preparation of 2,6,4'-Trimethoxy 4-Amino Azobenzene - For this product, diazotized 4-anisidine was coupled with dimethoxy aniline:



The diazo compound was prepared by dissolving 4.0 gms of 4-anisidine (about 0.033 mole) with 40 or 50 ml of water containing 8.2 ml of 10N HCl (0.082 mole) and 30 or 40 gms of crushed ice, and stirring the resulting cold solution during dropwise addition of 16.4 ml of 2N $NaNO_2$ (about 0.033 mole). After 10 minutes' stirring, a very slight excess of nitrous acid was destroyed by addition of a little dissolved sulfamic acid, and the diazo solution was treated with decolorizing carbon and filtered.

The filtrate was dropped, with stirring, into a slurry obtained by adding 25 ml of 4N sodium acetate (0.1 mole) to a solution of 5.0 gms (0.033 mole) of dimethoxy aniline in 16.5 ml of 2N HCl and 25 ml of water. The volume of the reaction mixture was then increased to 500 ml and stirring was continued for approximately 2 hours, after which 200 ml of 25% W/V NaCl solution were added, and the bright-red azo compound separated by filtration. The crude material was purified by solution in HCl and precipitation with sodium acetate. Thus purified, the product melted at

145.5°C (corrected); decomposition, with effervescence, occurred immediately after melting.

One gram was still further purified. It was dissolved in a mixture of 20 ml of benzene and 5 ml of anhydrous ethanol, and the solution was filtered, then stirred during dropwise addition of 100 ml of low-boiling petroleum ether. Fine bright-red crystals were precipitated. These were filtered off, washed with a few portions of petroleum ether, and dried at 60°C. The fluffy red material melted sharply at 147°C (corrected), then decomposed. Analyses indicate that it was not the free base (although possibly its acetate); it was still quite impure, despite the sharp melting point.

Analytical Data.-

	Calculated for $C_{15}H_{17}N_5O_3$	Calculated for $C_{15}H_{17}N_5O_3 \cdot C_2H_4O_2$	Found
% Carbon	62.70	58.78	56.43 (56.80)
% Hydrogen	5.96	6.09	5.71 (5.58)
% Nitrogen	14.63	12.10	11.93 (11.96)

Yellow Pigments from Acetoacetyl 2,4,6-Trimethoxy Anilide

Three yellow pigments were prepared from acetoacetyl trimethoxy anilide and three bases commonly used for such pigments: 3,3'-dichlorbenzidine (DCB), meta nitro para toluidine* (MNPT), and para chloro ortho nitro aniline (PCONA).

Yellow pigments from benzidine and substituted benzidines, such as DCB, are known as benzidine yellows. Similar pigments

* That is, 3-nitro 4-amino toluene

from monoamino compounds such as MNPT and PCONA are called Hansa yellows.

These pigments are used in two important ways. One use is for dyeing cloth, by the use of a dispersion of the pigment in a water-in-oil emulsion, the oil phase of which contains a thermo-setting resin. The cloth is printed with the pigment-bearing vehicle, then "cured." In the curing process the resin is "set" and the pigment is thoroughly bonded to the fabric. This method of dyeing and printing was developed by the Aridye division of Interchemical Corporation.

The other use of yellow azoic pigments is for paints and oil-base printing inks of the conventional type.

In either case, it is desirable that the pigment exhibit good lightfastness and be free from "solvent bleed" - that is, while dispersible in the vehicle, it should not dissolve in it or in organic liquids in general (especially dry-cleaning fluids). The benzidine yellows as a class are poor on the first score, the Hansa yellows on the second.

Method of Preparation - The method of preparation was essentially the same for each of the three pigments made. As an example, preparation of a pigment from 0.01 mole of DCB is described. The method was adapted from directions given in a recent patent (33).

For the tetrazotization, 0.01 mole of dichlorbenzidine is stirred with 25 ml of 2N HCl (0.05 mole) for 1 1/4 hours.

Then 50 gms of crushed ice and 200 ml of water are added. The mixture is stirred until most of the ice melts, when 10 ml of 2N $NaNO_2$ (0.02 mole) are added, in one portion. Stirring is continued for half an hour, then for another 15 minutes after addition of a little decolorizing carbon and activated silica. Finally, excess nitrous acid is destroyed with sulfamic acid and the solution filtered.

Meanwhile, a slurry of the coupling component has been prepared. A solution of 0.02 mole of the anilide in 11 ml of 2N NaOH (0.022 mole) and 15 ml of 4N sodium acetate (0.06 mole) is stirred for fifteen minutes with a little decolorizing carbon and activated silica, and filtered. Then the filtrate is stirred during dropwise addition of 11 ml of 2N HCl (0.022 mole).

The tetrazo solution is dropped into the slurry, with stirring, over a period of about an hour, and stirring is continued for four hours longer. Then the azo compound is filtered off, washed with several portions of water, and dried in vacuo over sulfuric acid. The yield is about 90%.

The long period of stirring and the method of drying the pigment, in vacuo over sulfuric acid, is used to leave it in a soft, finely divided condition, so that it is readily dispersible and gives full color value.

<u>Preparation of Ice Colors</u>

<u>General Discussion</u> - An ice color is one type of ingrain dye, which results when an insoluble azo compound is formed

within a textile fiber (usually cotton or staple fiber rayon) by reaction between a coupling component, usually phenolic, and a diazo compound.

A total of 129 ice-color dyeings was made, some from compounds whose preparation has been described and some from similar compounds used commercially. One object of the dyeings was to compare colors in which the coupling component was the 2,4,6-trimethoxy anilide of BON with colors from similar arylides. Another was to compare colors in which trimethoxy aniline was the base with some from other bases - especially ortho and para anisidine. Finally, a comparison was desired of colors from 2,6-dimethoxy 4-benzoylamino aniline and 2,6,4'-trimethoxy 4-amino azobenzene with colors from some of the commonly used ice-color bases, especially the so-called "blue bases" of commerce.

Sample pieces of all the colors obtained are mounted on the card forms in the appendix.

The general method of dyeing with ice colors has two steps. First, the fabric is impregnated with a solution of the coupling component in strong caustic. This solution contains turkey red oil (sulfonated castor oil) which assists in penetration of the fabric by the solution; sometimes other wetting agents are used along with or instead of turkey red oil.

In the second step, the impregnated cloth (which may be dried or not beforehand) is acted upon by a suitably buffered diazo solution. After thorough rinsing in cold water, the dyeing is completed by washing the cloth in a hot soap and soda bath.

To get good dyeings by this basically simple procedure is actually a rather complex process. In the first place, the cloth has to be carefully prepared before impregnation, to remove starch or other size which may be present, and to make the fibers absorbent. Then, individual differences of the compounds involved must be considered. The coupling components differ in tinctorial strength, affinity for the textile fiber, coupling ability, solubility, etc. The quantities of base and turkey red oil required differ from one coupling component to another, and the requirement has little relation to molecular weight. Similarly, the diazo compounds vary in tinctorial strength, stability to heat and light, coupling ability, optimum pH of coupling, etc. The best method of diazotizing a base to get a diazo compound is not the same in every case. Finally, after-treatment of the dyed cloth is not entirely uniform. Usually the cloth is washed in a boiling soap and soda bath, but certain azoic combinations must not be heated above about 70°C.

Fortunately, the large dye companies have published detailed instructions for ice-color dyeing (34, 35); in addition, the BON arylides have been in general use for so long that some non-commercial manuals on dyeing also give explicit directions (36). Most details of the procedure were obtainable, either directly or by analogy, from these sources. These details, constitutions of the dye intermediates, etc, are given in the subsections which follow.

Preliminary Treatment of Cloth to be Dyed - The cloth used was a rather tightly twisted white cotton gabardine, the only kind easily available at the time the first dyeings were made. A fabric with less twist and more loosely woven, such as cotton sheeting or broadcloth, would have offered less technical difficulty.

The first 119 dyeings were made without removal of a starch finish present on the cloth when bought. This finish proved to be resistant to hydrolysis with pancreatin, diastase, and various commercial amylolytic enzymes (probably because the starch inside the fibers or threads was not in contact with the enzymes), as well as to attempts at hydrolysis with acid. In a number of experiments with dilute sulfuric and hydrochloric acid at various temperatures and in various concentrations it proved to be impossible to hydrolyze the starch without tendering the cloth.

About a third of the dyeings on this un-desized cloth were uneven or dull. At the time the dyeings were made these defects were attributed to the presence of the starch, but it now seems more likely that they were due to other factors (such as poor control of pH in the diazo solutions, poor coupling ability of the diazo compounds or coupling components concerned, etc).

At any rate, an effort to discover a satisfactory method of removing the starch completely was continued. The writer is indebted to Mr. T. G. Sloan, of the research department of Rohm and Haas Company, for samples of Rhozyme DX and Triton W-30, used in the final successful method for removal of starch, as well as for directions for using those materials and for the suggestion that their use be followed by treatment with 1% NaOH solution.

Cloth used in the final ten dyeings (pages 18 and 19 in the appendix) was given the following preliminary treatment:

First the cloth was cut into lengths of a yard or less and notched for tearing into strips measuring about 4" x 32". Then it was soaked overnight at room temperature in a tap-water bath containing 1% Rhozyme DX (a soluble solid amylolytic enzyme preparation, probably containing inorganic salts or other materials to keep the solution slightly acid) and 0.25% Triton W-30 (a wetting agent to assist in penetration of the cloth by the enzyme).

Next the cloth was immersed for one hour in boiling 1% NaOH solution and for 8 hours in 5% soda ash solution. The NaOH removes remaining starch and starch hydrolysate from the cloth; the long boil in soda ash is intended to make the tightly twisted threads more absorbent and to remove bits of cottonseed hull, waxes, and other such materials which may be present on the fibers. For these alkaline boils the cloth was divided into small batches so that it could be completely immersed, since the cotton would be tendered through air oxidation if exposed to air in the presence of hot alkali.

During the alkaline boils the cloth became somewhat dark, probably from iron compounds or other impurities in the alkaline solutions. Therefore it was bleached by piece-wise immersion for 30-60 seconds in a boiling HCl-oxalic acid solution (25 ml of concentrated HCl and 42 gms of oxalic acid per liter of distilled water). Finally, the cotton pieces were rinsed successively in distilled water, 1% Na_2CO_3 in distilled water, and finally in enough distilled water to remove practically all the Na_2CO_3. The pieces were then air-dried at room temperature and torn into strips.

For the cloth used in the bulk of the dyeings, the preliminary treatment started with a 12-hour boil in 5% soda ash and was otherwise like the above. An alkaline boil under pressure is a preferred preliminary treatment (37), but this was not possible.

Impregnation of Cloth with Coupling Components - This part of the dyeing method, like the preliminary treatment of the cloth, differed somewhat in the case of the last dyes.

In the bulk of the dyeings, the cloth was soaked in solutions of the coupling components - known as padding solutions - for 1 1/2 to 2 hours. All the pieces impregnated with a given arylide were soaked at the same time, so as to expose all to a solution of the same concentration. They were agitated several times and twice taken out of the solution and put back in a different order, so as to impregnate the pieces as evenly as possible. After the soaking, the pieces were individually wrung out, wrapped in paper toweling in such a way that the entire surface areaof the cloth was in contact with the paper, and gently squeezed. This procedure resulted in retention by the cloth of 60 to 70% of its own weight of liquid.

After impregnation, or padding, in this way, the pieces were dried and fastened on glass holders before immersion in the diazo solutions for formation of the dye.

The final dyeings were fewer, so that only one or two pieces needed to be soaked in each padding solution. Fifteen minutes was found to be a quite sufficient length of time for the soaking. After impregnation the pieces were put through a small hand-operated clothes wringer. The cloth retained about the same weight of liquid with this handling as when squeezed with paper toweling. Finally, instead of being dried, the pieces were thoroughly rinsed in 10% NaCl solution, then immersed immediately in the diazo solution.

Rinsing in salt solution is probably preferable to drying, at least for small-scale operations. It has the advantage of removing any of the padding solution which adheres to the outside of the cloth, while presence of the salt prevents the coupling component within the fiber from being washed out. Immediate coupling, without drying, has the advantage that carbon dioxide or acid fumes in the atmosphere are not given a chance to react with the naphtholate on the cloth. The sodium salt of the arylide couples much more readily than the free arylide, so drying in the presence of carbon dioxide may spoil the dyeing.

The method of dissolving the naphthols was the hot, or turkey red oil, method described on page 4 of "DuPont Naphthanil and Naphthanil Diazo Colors." The naphthol is pasted free of lumps with the necessary quantities, first, of turkey red oil and then of 11N NaOH. The resulting pasty mass is dissolved in a suitable volume of hot water; boiling may be necessary to bring about solution. Then the hot solution is diluted with cold water to the final volume. Formaldehyde is added when the solutions are to be kept for some time, but was not necessary for these dyeings.

Table I on page 42 shows the weights of the various arylides used for 1 liter of padding liquor, together with the quantities of turkey red oil, NaOH solution, and hot water which were necessary to get them into solution. The quantities of naphthol were varied, as indicated, because of variations in tinctorial strength and affinity for the fiber; an effort was made to choose such quantities that the final dyed pieces would have a fairly uniform appearance. The basis for deciding what quantities to use was chiefly the appearance of dyed pieces in the DuPont publication referred to, although a few test dyeings were made, especially with the new intermediates.

Table I - Ice-Color Coupling Components: Names, Constitutions, and Composition of Padding Solutions

Name of Arylide	Constitution: Base from Which Derived	Quantities for One Liter of Impregnating Solution			
		Gms of Arylide	Ml T-R Oil	Ml 11N NaOH	Ml Hot Water
Naphthol AS	Aniline	15.1	23	23	130
" AS-D	2-Toluidine	15.1	23	23	130
" AS-TR	2-Methyl 4-Chlor Aniline	15.1	44	44	600
" AS-BO	1-Naphthylamine	7.6	16	16	100
" AS-SW	2-Naphthylamine	5	15	15	200
" AS-OL	2-Anisidine	15.1	23	23	130
" AS-2EA	2-Ethoxy Aniline	15.1	32	32	250
" AS-RL	4-Anisidine	10	25	25	200
" AS-TMA	2,4,6-Trimethoxy Aniline	15.1	38	38	300
" AS-ITR	2,4-Dimethoxy 5-Chlor Aniline	5	13	13	220
" AS-BG	2,5-Dimethoxy Aniline	5	13	13	100
" AS-DEA	2,5-Diethoxy Aniline	5	13	13	200
" AS-G*	Benzidine	15.1 10	30 20	30 20	200 200

* Naphthol AS-G, so called, is not a naphthol at all, being the di-acetoacetyl derivative of benzidine. The second set of figures for this intermediate indicates the composition of the bath used for Dye No. 120, which also contained 60 gms of Glauber's salt per liter. The first set applies to all the other dyeings with Naphthol AS-G.

Table I also gives the names of the bases from which the naphthols are derived. Note that the designations AS-TMA, AS-2EA, and AS-DEA are coined; the other names are those of commercial products.

Preparation of Developing Baths - While every diazotization is a problem in itself, and has its own set of optimum conditions like any other reaction, a rough classification of amines can be made on the basis of the general methods by which they are diazotized. The ice-color bases used for the dyeings described here fall into four main groups.

Some of the bases were bought as stabilized diazo compounds, and hence did not have to be diazotized. Developing baths were prepared from them by merely dissolving the commercial products (dry powders) in water, stirring them with a little decolorizing carbon and activated silica, and filtering. Although prepared in various ways, these materials are similar from the standpoint of use and have been classed together as Type A.

Of the bases which had to be diazotized, the first group, Type B, includes those which diazotize easily without side reactions. These were diazotized by the "direct" method - that is, $NaNO_2$ solution was added slowly to a cold solution of the base containing 2.5 mole parts of HCl until diazotization was complete. Excess nitrous acid was then destroyed with sulfamic acid, and the solution was decolorized with carbon black and activated silica, and filtered.

The second group, Type C, includes nitro and chloro anilines, which have a strong tendency to form diazo-amino compounds. In this case, diazotization is carried out by the "indirect" method - that is, all the $NaNO_2$ is added at the start, so that diazotization will be complete before extensive occurrence of any side reaction. Also, somewhat more acid is used than with Type B bases. Type C bases are not very strongly basic and it is difficult to form their amine salts. More acid is used for this reason, as well as to inhibit diazo-amino formation. To insure formation of the amine salt, and also to get the salt into a finely divided reactive form, the bases are heated with whatever volumes of acid and water are necessary to bring about solution, then cooled suddenly by addition of crushed ice. When the bases are not volatile in steam, and have high melting points, a suspension of the base in water is boiled and then the necessary acid is added. But bases which have low melting points, or which are volatile in steam (usually those with a nitro group ortho to the amino group), are first triturated with the acid. They should not be heated above about 80°C, even after formation of the salt; occasionally diazotization is carried out without complete solution of the salt having taken place.

The third group to be diazotized, Type D, consisted of three bases with a tendency toward self-coupling. They were diazotized in the same way as the Type C bases, indirectly and in presence of a considerable excess of acid, but it was not considered necessary to take as great precautions to bring about complete salt formation initially, since these compounds are fairly strong bases and salt formation could continue to occur as the diazotization proceeded. However, the hydrochloride of alpha naphthylamine (Fast Garnet B Base) is rather insoluble, so only half the acid was added initially; the hydrochloride was all dissolved before addition of the remaining acid and the crushed ice.

In all cases, the clarified diazo solution was made to a convenient volume, usually about 6 liters, and neutralized with sodium acetate, sodium bicarbonate, or sodium hydroxide before immersion of the padded pieces. The proper choice of neutralizing agent depends upon the optimum pH of coupling of the diazo compound concerned. The optimum pH is low, in general, for diazos from nitro and chloro anilines, high for those from methoxy substituted anilines. Diazos which couple readily do so at a low pH; those which have to be buffered with bicarbonate are likely to couple very slowly even at their optimum pH.

Unfortunately, trimethoxy aniline, 2,6-dimethoxy 4-benzoylamino aniline, and 2,6,4'-trimethoxy 4-amino azobenzene, of which only very small quantities were available - and whose diazo solutions were therefore quite dilute - are poor couplers. When the dyeings with trimethoxy aniline were made, this fact was not understood and proper precautions were not taken. The diazo solution was made to 6 liters with water. Coupling was very slow and was finally brought about, after the padded pieces had been in the diazo solution for about an hour, by addition of 10N NaOH. The naphthol was partially dissolved from portions of the cloth, especially after addition of the NaOH; the overall result was very uneven dyeings.

The solution of diazotized 2,6-dimethoxy 4-benzoylamino aniline, however, was made to only 1 liter, with 10% NaCl rather than with water, and neutralization was with $NaHCO_3$, which has no solvent action on the naphthols. About 15 minutes was sufficient to develop the colors fully, even though the developing bath was again quite dilute. Beautifully even dyeings were obtained.

The same procedure was followed with the trimethoxy amino azobenzene, but dilution with 10% NaCl resulted in precipitation of the diazo compound itself, which is rather insoluble, and the dyeings were again very unsatisfactory.

In the diazo baths from dianisidine, diamino diphenylamine, and 2- and 4-anisidine, the error of neutralizing with NaOH was made again. These would properly be neutralized with $NaHCO_3$.

Another error was made with the dyeings from dianisidine. In most cases, a too concentrated diazo solution did not matter, since the unreacted excess could be washed out of the cloth. Dianisidine, however, gives a tetrazo compound, so that it is possible for the molecule to couple at one end and not at the other. The diazo group at the other end of the molecule, if uncoupled, cannot be washed out, since it is a part of a large molecule within the fiber. Decomposition occurs in time, but the result is a dull, unsatisfactory color. For good results, the diazo and coupling component must be carefully balanced.

The diazotized dianisidine solution was in fact made too concentrated, and the result is seen in the uneven purplish brown appearance of dyes 94 to 98 on page 14 in the appendix. They should have been blue.

Dyeings with diamino diphenylamine and other diamines are subject to the same possibility of error, but this fact had been discovered by the time the five dyes from diamino diphenylamine were made. A dilute diazo solution was used, giving clear dyeings of good appearance (dyes 115 to 119 on page 17 in the appendix).

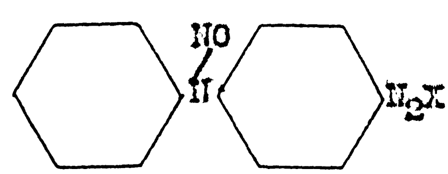
The solutions prepared from the stabilized diazos were also made more concentrated than necessary, 25 gms of material having been made to about 3 liters in each case. Since these are diazo compounds, no great harm was done, although the problem of washing the dyed pieces was made more difficult (the diazos decompose and their decomposition products coat the surface of the fabric and the walls of the containing vessels). It was discovered afterward that about 2.5 gms per liter is the usual concentration at which the stabilized blue bases are used.

Table II, on pages 49 and 50, gives constitutions of all the ice-color bases used in these dyeings, together with quantities of base, nitrite, acid, etc, which were used in preparing the developing baths.

Developing and Finishing the Dyed Pieces - As has already been indicated, the dyeings were completed by immersion of the impregnated pieces in the diazo baths, with occasional agitation, until the colors were completely developed. From 5 to 15 minutes was usually sufficient time.

Then the dyed pieces were thoroughly rinsed with water, first cold and then hot, and finished by immersion for at least an hour in a hot soap and soda bath (3.75% sodium oleate and 0.75% soda ash, W/V). The bath was heated to only 71°C for all dyes in which methoxy groups were present, to the boil for the others. Finally, the pieces were again rinsed with water and air-dried at room temperature.

Dyes 104 to 114, inclusive, prepared from stabilized diazos of "variamine"blue bases, had to be given a special finishing treatment. The variamine diazos are stabilized as nitroso-diazo compounds having the following basic structure



where X is a monovalent negative ion and either or both the benzene rings may bear substituents (33).

Table II - Ice-Color Bases: Names, Constitutions, Diazotization Types, and Quantities of Materials Used in Diazotization

Commercial Name of Bases or Diazo	Chemical Name of Base	Type	Quantities Used for Diazo Developing Bath						
			Gms Base	Ml Hot Water	Ml 10N HCl	Gms Ice	Ml 2N $NaNO_2$	Gms NaOAc	Ml 10N NaOH
Fast Red 2B	2-Anisidine	B	56.9		75	400	150		45
	2,4,6-Trimethoxy Aniline	B	9.1		12.5	25	25		9
	4-Anisidine	B	56.9		75	400	150		45
Fast Orange G	3-Chlor Aniline	B	12.6		25	400	50	10	
Fast Red KB	2-Methyl 5-Chlor Aniline	C	14.2	170	25	400	50	10	
Fast Scarlet 2G (or GG)	2,5-Dichlor Aniline	C	48.6	510	115	1200	150	62	
Fast Orange GR	2-Nitro Aniline	C	13.6	170	38	400	50	21	
Fast Red 2G (GG)	4-Nitro Aniline	C	40.8	510	115	1200	150	62	
Fast Red G (or GL)	2-Nitro 4-Methyl Aniline	C	15.2	170	38	400	50	21	
Fast Scarlet G (or GC)	2-Methyl 5-Nitro Aniline	C	15.2	170	38	400	50	21	
Fast Bordeaux GPR	2-Nitro 4-Methoxy Aniline (or like)	C	16.8	170	38	400	50	21	
Fast Red B	2-Methoxy 4-Nitro Aniline	C	50.4	510	115	1200	150	62	

Table II - Ice-Color Bases: Names, Constitutions, Diazotization Types, and Quantities of Materials Used in Diazotization

Commercial Name of Base or Diazo	Chemical Name of Base	Type	Quantities Used for Diazo Developing Bath: Gms Base*	Ml Hot Water	Ml 10N HCl	Gms Ice	Ml 2N $NaNO_2$	Gms NaOAc	Ml 10N NaOH
Fast Garnet B	1-Naphthylamine	D	14.3	100	25	250	50	10	
Fast Blue B	3,3'-Dianisidine	D	36.6	750	75	1200	150		45
Fast Blue Salt BBN	Similar to 2,5-Diethoxy 4-Benzoylamino Aniline	A	25						
Variamine Blue Salt RT	4-Amino Diphenylamine	A	25						
Variamine Blue Salt BD	Similar to 4'-Methoxy 4-Amino Diphenylamine	A	25						
Fast Black B	4,4'-Diamino Diphenylamine	D	8.7	125	12.5	200	25		7.5
	2,6-Dimethoxy 4-Benzoylamino Aniline	B	4.4		4.1	75	8.1		**
	2,6,4'-Trimethoxy 4-Amino Azobenzene	C	4.2	60	7.3	100	7.3		**

* Or stabilized diazo compound

** These were each neutralized with about 5 gms of $NaHCO_3$.

After coupling, the nitroso group has to be saponified off and reduced. This was accomplished in these dyeings by boiling the dyed pieces for about half an hour in 5% sodium sulfide solution. This treatment followed the usual rinses with water, and was followed by the usual soaping.

Lightfastness Tests and Results

Tests on Pigments - Samples of the three yellow pigments prepared from acetoacetyl trimethoxy anilide were submitted to Interchemical Corporation, New York, for testing as Aridye and oil print pigments.

All appear to be unsatisfactory for either application. Inks made up in an oil vehicle hardened too rapidly for testing to be completed, while the pigments exhibited relatively poor lightfastness when printed on cloth with Aridye resin.

Tests on Ice Colors - Lightfastness tests on the first 110 ice colors were made by Mr. James Chapman of Ault and Wiborg, Cincinnati. The last ten dyes were tested by the Rit Products Company, Chicago.

Numbers have been used to indicate results of the lightfastness tests. The numbers have the following significance:

1 - Poor, or definite change on 2 hours' exposure*

2 - Poor, or definite change on 4 hours' exposure

3 - Moderate to poor, or definite change on 5 hours' exposure

* In the fadeometer

4 - Fairly good, or definite change on 30 hours' exposure

5 - Good, or definite change on 60 hours' exposure

6 - Very good, or definite change on 120 hours' exposure

7 - Very good, or definite change on 240 hours' exposure

8 - Excellent, or definite change on 300 or more hours' exposure

This rating scale is copied from the DuPont publication referred to.

Numbers are quoted in the lightfastness-rating column of the card-forms in the appendix for such of the dyes as appear in the DuPont book; for the others, they were estimated comparatively or directly from the appearance of the strips exposed in the fadeometer. Such estimates are necessarily very rough, since the test strips show the appearance after a definite uniform period of time and not at the time of the first "break" in the color.

Where two numbers are given, the rating is of course somewhere between the ratings indicated by the numbers.

DISCUSSION OF RESULTS

The experimental results present several interesting features.

One of the most interesting, to the writer, has been the fact that he was able to work on a scale which to the early workers with phloroglucinol would have seemed lavish indeed. The largest quantity of phloroglucinol mentioned in any one of the references quoted from the literature was 30 grams, whereas in one experiment reported here over 700 grams was used, and use of 150 grams or more was common. Another product which was formerly so costly that few experimenters could afford to work with it has come to be potentially so abundant that it is important to know more about it.

Working with the knowledge that any quantities of materials likely to be needed will be available, while not necessarily conducive to development of a fine technique, does permit repetition of experiments when necessary, and encourage the testing of ideas which might in more austere circumstances be dismissed as too speculative.

A few specific comments on some of the results seem to be in order:

<u>Methylation of Phloroglucinol</u> - The procedure given for preparing phloroglucinol ethers, while it works fairly well, could probably be improved upon. Large amounts of dimethyl ether are formed in the first stages of the methylation, so that much of the methyl sulfate is used to methylate methanol rather than phloroglucinol. This might be prevented by diluting the methanol solution with the right amount of water, but it may well be true that relatively anhydrous conditions are necessary for extensive methylation of the phloroglucinol. This point was not investigated. It seems possible that

methyl sulfate alone would be a suitable methylating agent, at the right temperature, although at its own boiling point it causes decomposition and resinification of the phloroglucinol.

The melting points given in the experimental part for dimethoxy phenol and methoxy resorcinol are from 4 to 5° higher than those given in the literature sources cited.

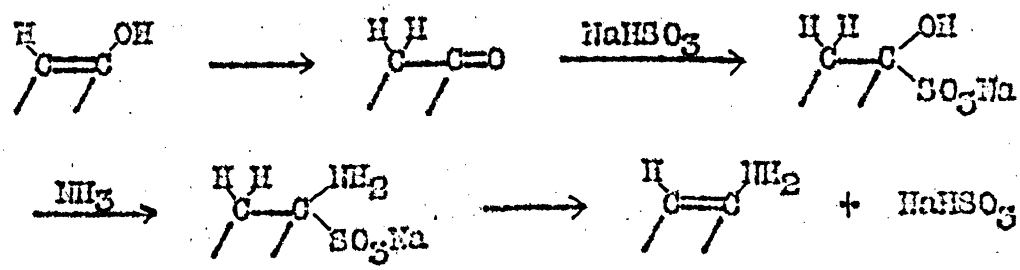
Preparation of Trimethoxy Aniline - Coupling of trimethoxy benzene, the basis of the experimental method for obtaining trimethoxy aniline, is interesting historically because it formed part of the evidence advanced by K. H. Meyer (28, 39, 40) to disprove the hypothesis of Kekulé (41) and Dimroth (42) that coupling to phenols and amines necessarily proceeds through intermediate formation of diazo ethers and diazoamino compounds, which rearrange to the final azo compounds. Meyer's view was that coupling takes place through intermediate addition to the conjugated double bonds of the aromatic ring (or similar structure, such as an acetoacetyl group). This is now fairly generally accepted, although modified by Karrer's idea that ammonium or oxonium compounds are involved in some cases (43, 40).

The reduction of 2,4,6-trimethoxy azobenzene 4'-sulfonic acid, also part of this synthesis, was carried out with sodium hyposulfite because of the convenience of using that reagent. However, the yield was never greater than 60% in the half dozen or so preparations of trimethoxy aniline.

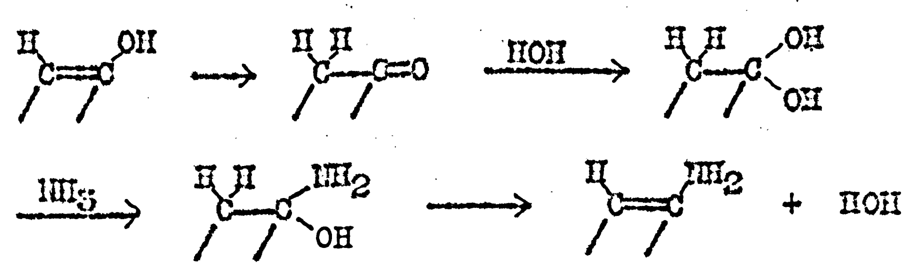
The poor yield was doubtless due to side reactions. One which is known to occur in reductions with hyposulfite is formation of sulfaminic acids (44). Reduction with zinc, tin, or iron should give better results.

<u>Ammonolysis Reactions</u> - In the discussion of the Bucherer reaction already cited (32) the case of phloroglucinol is scarcely mentioned, perhaps because the reaction goes so easily with phloroglucinol that use of ammonium sulfite is unnecessary. The mechanism for formation of phloramine from phloroglucinol is no doubt essentially the same as for formation of beta naphthylamine from beta naphthol, with intermediate addition of water instead of bisulfite to a carbonyl group.

For the latter reaction the following mechanism has been well established (45, 32):



The analogous mechanism for the more active phloroglucinol is:



The really interesting result of the ammonolysis experiments is that ammonolysis of phloroglucinol dimethyl ether can be made to occur. This probably indicates that the two methoxy groups have a powerful enough activating effect to bring about the same keto-enol tautomerism that exists in phloroglucinol, although obviously the enol form is much more strongly predominant in the ether than in phloroglucinol itself.

Shades of the Dyes - The colors obtained with all the intermediates were unexpected and disappointing. The presence of two methoxy groups ortho to one side of an azo group did not deepen the shade or increase the tinctorial strength of the dyes to as great an extent as had been expected.

Most of the dyes prepared from trimethoxy aniline base, as will be observed from the samples on the card forms, are definitely bluer than the adjoining dyes from 2- and 4-anisidine; but greater deepening of the shade had been expected and production of definitely blue colors would not have been surprising.

Deepening of the shade is even less pronounced in the case of dimethoxy benzoylamino aniline (see dyes 121 to 125, page 18 in the appendix). These dyes are somewhat deeper than corresponding dyes from 2-anisidine, but they do not approach in depth the blues obtained from the similar fast blue salt BBN (dyes 99 to 103, page 15 in the appendix) in which alkoxy groups are in the 2,5-positions.

The BOH derivative of trimethoxy aniline actually gives as light shades as Naphthol AS itself - lighter in a few cases. Since most substituents deepen the shade more or less, or increase the tinctorial strength, this effect was particularly surprising. The same effect was observed in colors from the acetoacetyl derivative.

The four intermediates already mentioned give bright attractive shades. This is not the case with trimethoxy amino azobenzene, however (see dyes 126 to 129, pages 18 and 19 in the appendix), which gives brownish unattractive colors, at least in the concentrations used. This defect is enough by itself to negate application of trimethoxy amino azobenzene as an ice-color base, and probably for most other purposes. Some of the effect is due to the poor solubility of the base, however, and it is possible that better results would be achieved if it were used as a base for acid wool dyes.

The colors from dimethoxy benzoylamino aniline are bright and clear enough (particularly the yellow, dye 120), but the poor lightfastness denies them commercial possibilities. However, this intermediate, too, might be of interest as a base for acid wool dyes.

Lightfastness of the Dyes - Lightfastness of all dyes in which trimethoxy aniline was the base was very poor. This result was not altogether unexpected, since it is usually true of anisidines, and might be truer of a base in which the substituted phenyl group was still more highly electro-negative. It was supposed that the steric effects of the methoxy groups in the 2,4,6-positions might offset the other effect to some extent, but that they did not was not surprising.

Dyes in which the trimethoxy anilide of BON was the coupling component also did not exhibit unusual fastness, but this may be due in part at least to faulty dyeing technique. As might be expected, they proved much better than those in which trimethoxy aniline was the base. In the following tabulation are gathered lightfastness ratings for the dyes from Naphthol AS-TMA and the three naphthols most nearly comparable with it:

Fast Color Base Present in Dye	Lightfastness Ratings for Dyes, Listed under Naphthols Present			
	AS-OL	AS-RL	AS-TMA	AS-ITR
Orange G	6-5	6	5-4	7-6
Red KB	6	7-6	7-6	7
Scarlet 2G	6	7-6	6	7-6
Orange GR			6-5	7-6
Orange R	5	5	5-4	7-6
Red 2G	-	[illegible]	6-5	7-6
Red G	6	7-6	6	7-6
Scarlet G	5-4	5-4	5-4	5-4
Bordeaux GPR	7-6	6	5-4	6-5
Red B			5-4	5-4
Garnet B	5	6-5	5-4	6-5
Blue B	4	5-4	4-3	4-3
Blue BBN	6	5-4	6-5	6-5
Variamine Blue RT	7-6	5-4	4-3	6-5
Variamine Blue BD	6-5	6-5	4-3	5-4
Black B	7-6	7-6	5-4	7

The dyes from Naphthol AS-TMA rank "fairly good" to "very good." Nine combinations were equal to the corresponding ones from a comparable intermediate, and two were superior, although thirty-one were inferior. In general, this intermediate may be said to give ice colors quite comparable in quality with many which are used commercially, although slightly inferior to some others. If its dyeing idiosyncrasies were fully investigated and utilized, Naphthol AS-TMA might well look much better than it does here as an ice-color intermediate.

Lightfastness of dyes from 2,6-dimethoxy 4-benzoylamino aniline and 2,6,4'-trimethoxy 4-amino azobenzene was very poor - definitely inferior to that of dyes from similar intermediates. As an explanation, an interesting possibility suggests itself. In both cases, the final dyes have two methoxy groups ortho to an azo group from the same side (that is, in positions 2 and 6 from the azo). Although one group has a favorable effect, and doubtless for steric reasons, two may well cause such strain that the molecule is made more vulnerable, rather than less, to oxidative attack. This idea may also help to explain the poor lightfastness, already discussed, of the dyes from trimethoxy aniline.

SUMMARY

(1) A new method has been described for preparation and isolation of good yields of the methyl ethers of

phloroglucinol. The three others are prepared simultaneously by refluxing phloroglucinol dihydrate with methyl sulfate in methanol, and separated through solubility differences in water, aqueous alkali, benzene, and diethyl ether.

(2) A new compound, 2,4,6-trimethoxy aniline, and three of its condensation products have been prepared and characterized. Trimethoxy aniline was prepared by coupling trimethoxy benzene with diazotized sulfanilic acid in dilute acetic acid solution and reducing the product.

(3) 3,5-Dimethoxy aniline has been prepared by two methods not previously used: (a) from phloramine by processes of acetylation, methylation, and hydrolysis; and (b) from 3,5-dimethoxy phenol through ammonolysis by the Bucherer method. In the course of the preparation from phloramine the new compounds 5-acetylamino resorcinol and acetyl 3,5-dimethoxy anilide were prepared and characterized.

(4) A new dye intermediate, dimethoxy benzoylamino aniline (believed to be 2,6-dimethoxy 4-benzoylamino, but possibly 2,4-dimethoxy 6-benzoylamino) has been prepared from 3,5-dimethoxy aniline and characterized. The preparative method involved coupling dimethoxy aniline with diazotized sulfanilic acid, benzoylating the product, and reducing the benzoyl derivative.

(5) A new dye intermediate, trimethoxy amino azobenzene (believed to be 2,6,4'-trimethoxy 4-amino, but possibly 2,4,4'-trimethoxy 6-amino), has been prepared by coupling

3,5-dimethoxy aniline with diazotized 4-anisidine, and characterized.

(6) Acetoacetyl 2,4,6-trimethoxy anilide has been partially evaluated as a coupling component for azoic pigments by preparing and having tested three pigments in which it was the coupling component.

(7) 2,3-Hydroxy naphthoyl-2',4',6'-trimethoxy anilide (the 2,4,6-trimethoxy anilide of beta oxy naphthoic acid) has been partially evaluated as an ice-color coupling component by preparing and getting lightfastness tests on a series of ice-colors in which it was used.

(8) 2,4,6-Trimethoxy aniline, dimethoxy benzoylamino aniline, and trimethoxy amino azobenzene have been partially evaluated as ice-color bases by preparing and getting lightfastness tests on a series of ice colors in which they are used.

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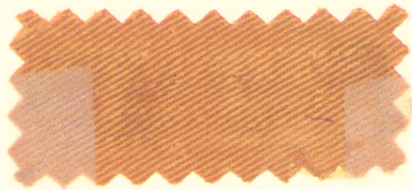
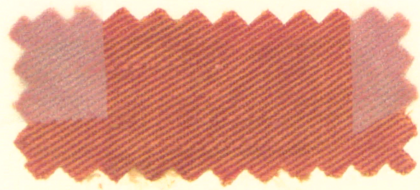
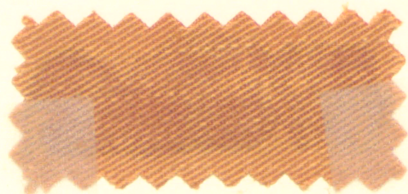
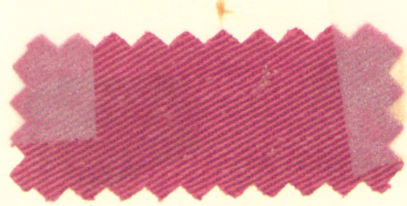
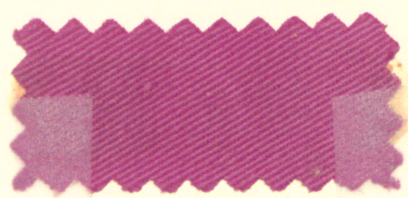
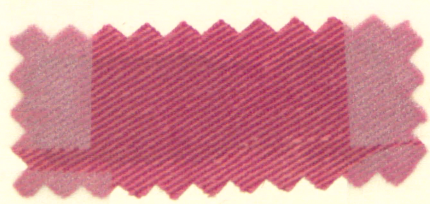
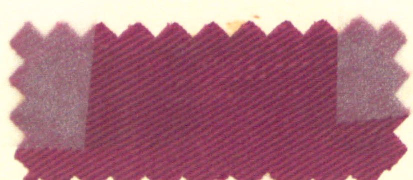
APPENDIX: MOUNTS OF DYED COTTON PIECES

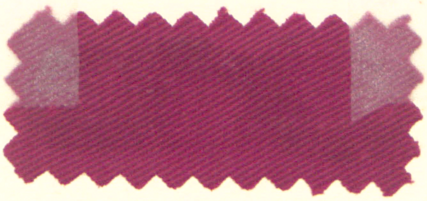
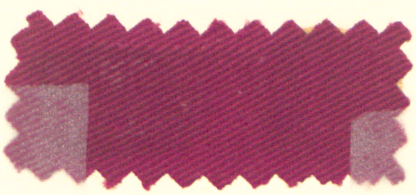
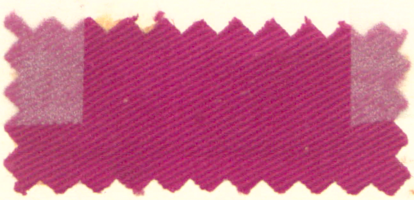
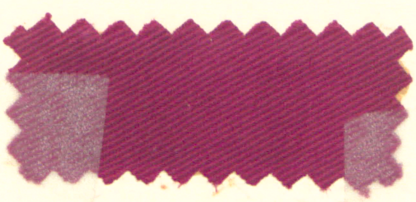
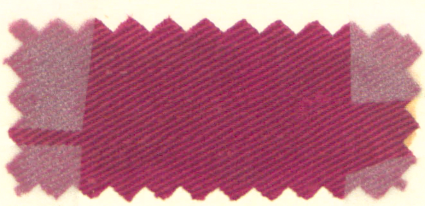
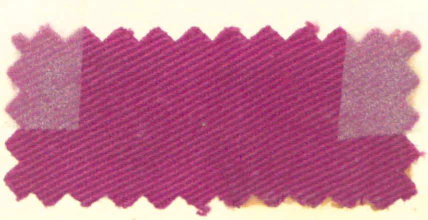
Shade, Constitution, and Lightfastness Ratings for Ice-Color Combinations

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
1	1	4-3	FAST RED 2B BASE with NAPHTHOL AS-G	
2	1	4-3	TRIMETHOXY ANI-LINE with NAPHTHOL AS-G	
3	1	4-3	4-ANISIDINE with NAPHTHOL AS-G	
4	1	4-3	FAST RED 2B BASE with NAPHTHOL AS	
5	1	4-3	TRIMETHOXY ANI-LINE with NAPHTHOL AS	
6	1	4-3	4-ANISIDINE with NAPHTHOL AS	
7	1	4	FAST RED 2B BASE with NAPHTHOL AS-D	

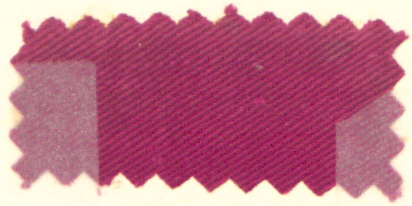
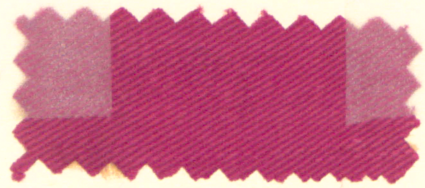
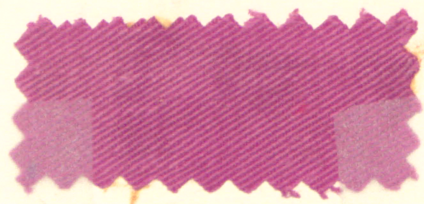
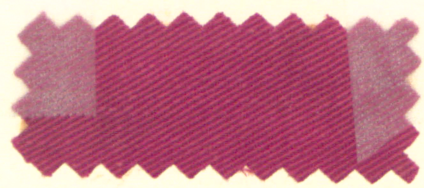
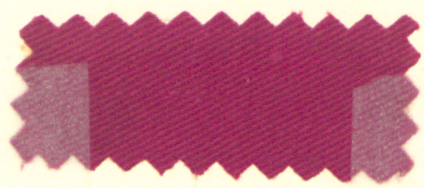
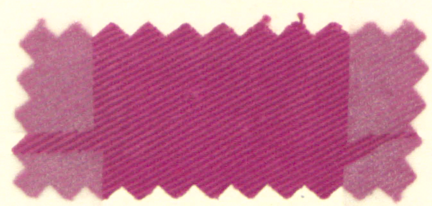
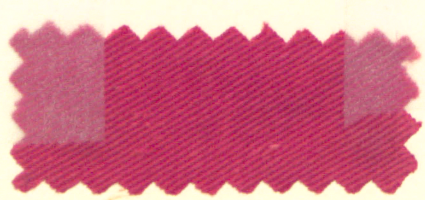
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
8		TRIMETHOXY ANILINE with NAPHTHOL AS-D	1	4
9		4-ANISIDINE with NAPHTHOL AS-D	1	4
10		FAST RED 2B BASE with NAPHTHOL AS-TR	1	4
11		TRIMETHOXY ANILINE with NAPHTHOL AS-TR	1	4-3
12		4-ANISIDINE with NAPHTHOL AS-TR	1	4
13		FAST RED 2B BASE with NAPHTHOL AS-BO	1	4
14		TRIMETHOXY ANILINE with NAPHTHOL AS-BO	2	4-3

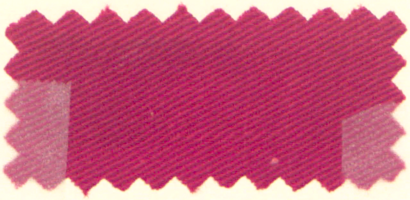
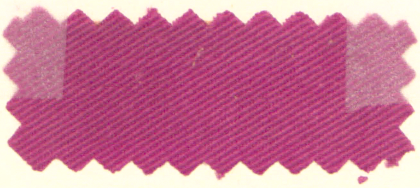
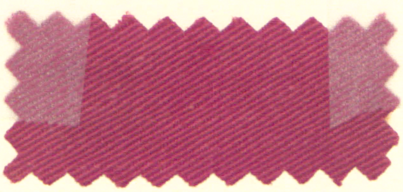
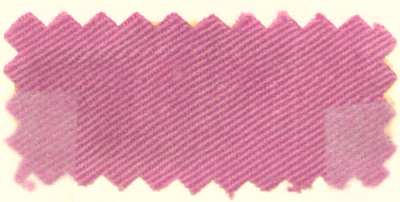
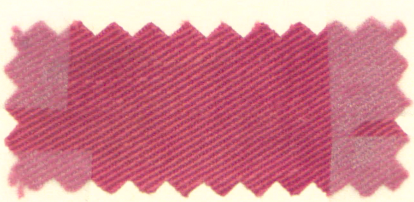
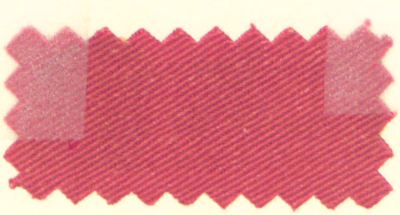
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
15	2	4	4-ANISIDINE with NAPHTHOL AS-BO	
16	2	4	FAST RED 2B BASE with NAPHTHOL AS-SW	
17	2	4-3	TRIMETHOXY ANILINE with NAPHTHOL AS-SW	
18	2	4	4-ANISIDINE with NAPHTHOL AS-SW	
19	2	5-4	FAST RED 2B BASE with NAPHTHOL AS-OL	
20	2	4-3	TRIMETHOXY ANILINE with NAPHTHOL AS-OL	
21	2	5-4	4-ANISIDINE with NAPHTHOL AS-OL	

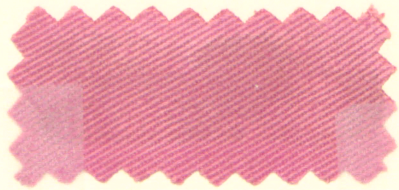
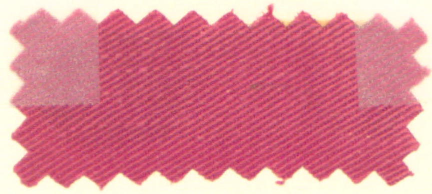
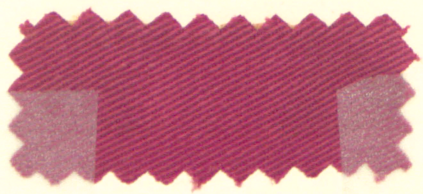
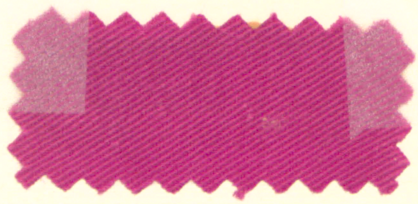
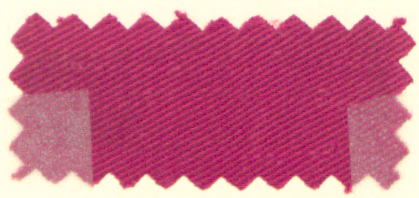
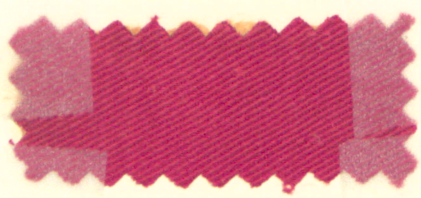
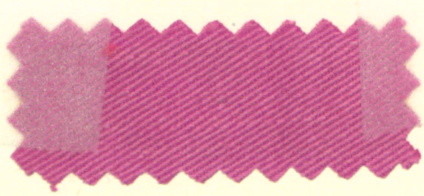
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
22		FAST RED 2B BASE with NAPHTHOL AS-2EA	2	5-4
23		TRIMETHOXY ANILINE with NAPHTHOL AS-2EA	2	4-3
24		4-ANISIDINE with NAPHTHOL AS-2EA	2	4
25		FAST RED 2B BASE with NAPHTHOL AS-RL	2	4
26		TRIMETHOXY ANILINE with NAPHTHOL AS-RL	2	4-3
27		4-ANISIDINE with NAPHTHOL AS-RL	3	4-3
28		FAST RED 2B BASE with NAPHTHOL AS-TMA	3	4-3

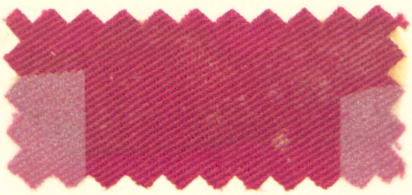
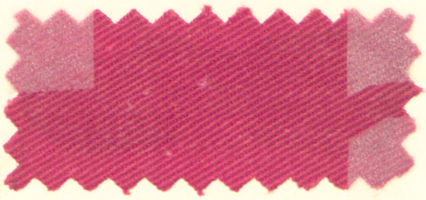
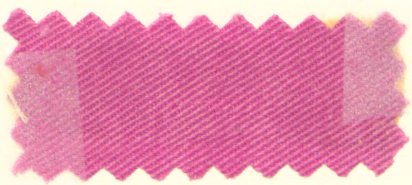
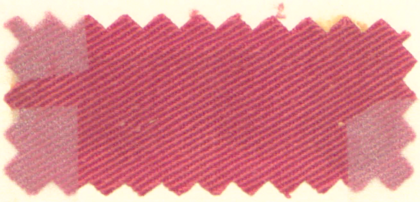
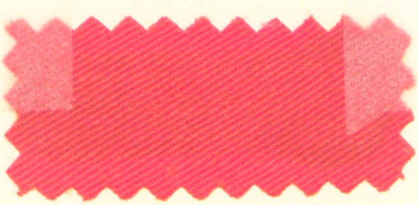
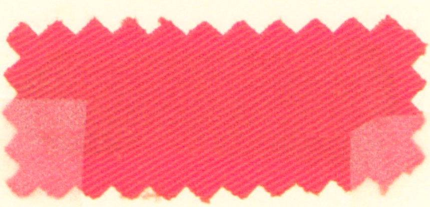
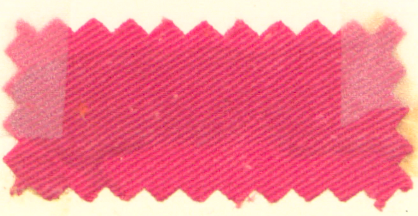
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
29	3	4-3	TRIMETHOXY ANILINE with NAPHTHOL AS-TMA	
30	3	4-3	4-ANISIDINE with NAPHTHOL AS-TMA	
31	3	4-3	FAST RED 2B BASE with NAPHTHOL AS-ITR	
32	3	4-3	TRIMETHOXY ANILINE with NAPHTHOL AS-ITR	
33	3	4-3	4-ANISIDINE with NAPHTHOL AS-ITR	
34	3	5-4	FAST RED 2B BASE with NAPHTHOL AS-BG	
35	3	4-3	TRIMETHOXY ANILINE with NAPHTHOL AS-BG	

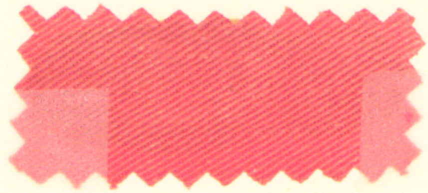
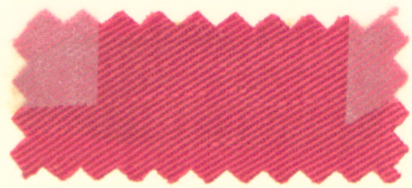
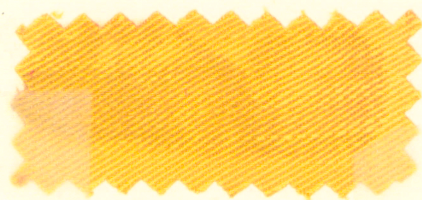
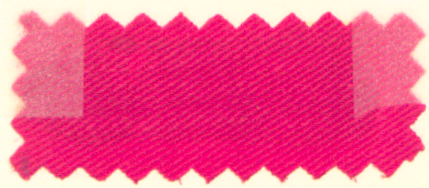
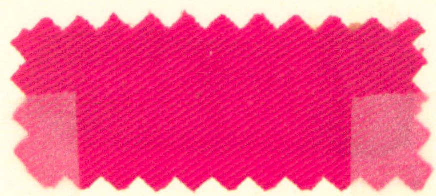
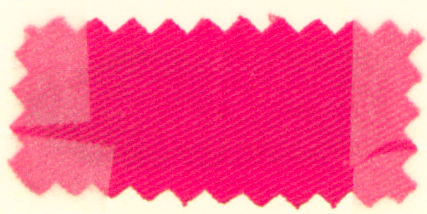
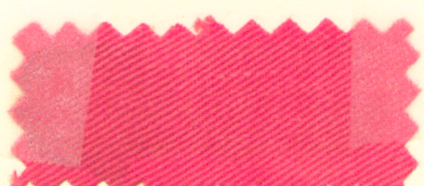
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
36		4-ANISIDINE with NAPHTHOL AS-BG	3	4
37		FAST RED 2B BASE with NAPHTHOL AS-DEA	3	4-3
38		TRIMETHOXY ANILINE with NAPHTHOL AS-DEA	3	4-3
39		4-ANISIDINE with NAPHTHOL AS-DEA	3	4-3
40		FAST ORANGE G BASE with NAPHTHOL AS-D	4	6-5
41		FAST ORANGE G BASE with NAPHTHOL AS-OL	4	6-5
42		FAST ORANGE G BASE with NAPHTHOL AS-RL	4	6

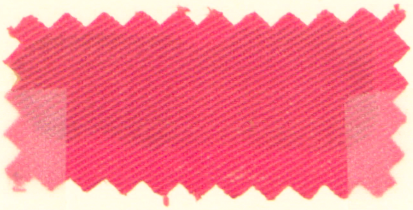
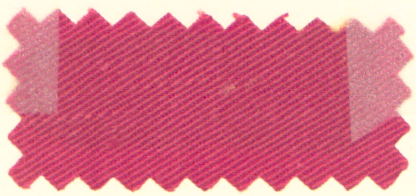
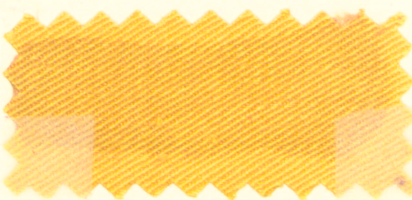
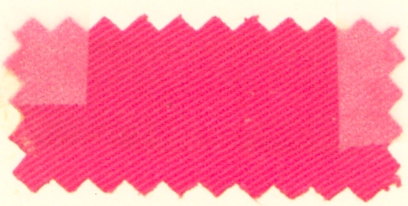
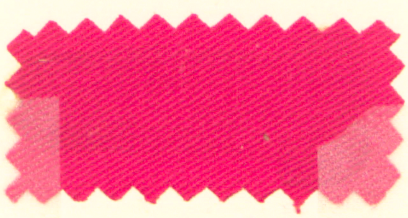
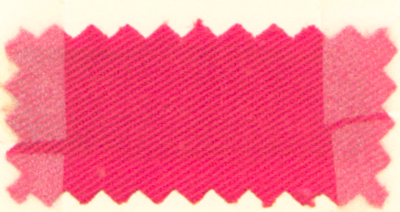
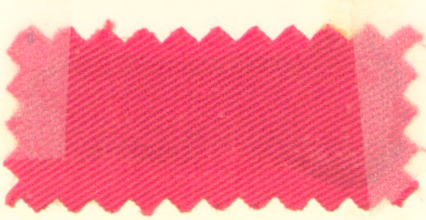
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
43	4	5-4	FAST ORANGE G BASE with NAPHTHOL AS-TMA	
44	4	7-6	FAST ORANGE G BASE with NAPHTHOL AS-ITR	
45	4	5-4	FAST RED KB BASE with NAPHTHOL AS-G	
46	4	6	FAST RED KB BASE with NAPHTHOL AS-D	
47	4	6	FAST RED KB BASE with NAPHTHOL AS-OL	
48	4	7-6	FAST RED KB BASE with NAPHTHOL AS-2EA	
49	4	7-6	FAST RED KB BASE with NAPHTHOL AS-RL	

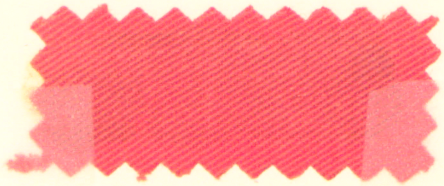
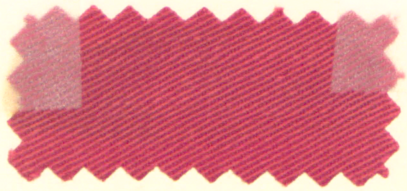
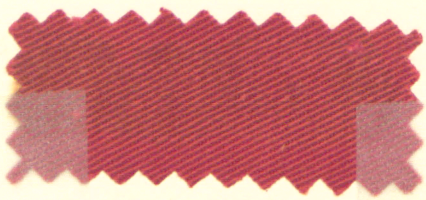
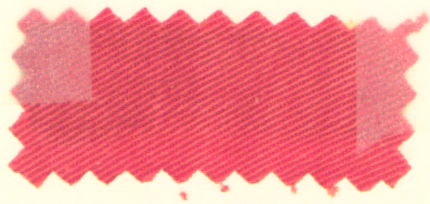
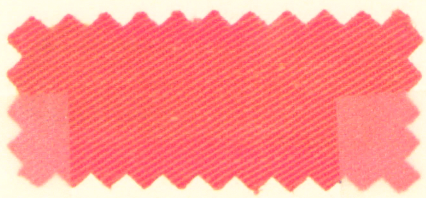
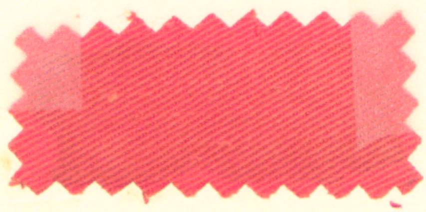
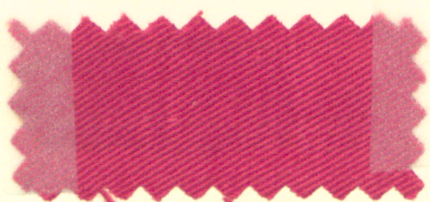
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
50		FAST RED KB BASE with NAPHTHOL AS-TMA	4	7-6
51		FAST RED KB BASE with NAPHTHOL AS-ITR	4	7
52		FAST SCARLET 2G BASE with NAPHTHOL AS-G	4	5-4
53		FAST SCARLET 2G BASE with NAPHTHOL AS	5	5
54		FAST SCARLET 2G BASE with NAPHTHOL AS-OL	5	6
55		FAST SCARLET 2G BASE with NAPHTHOL AS-2EA	5	6
56		FAST SCARLET 2G BASE with NAPHTHOL AS-RL	5	7-6

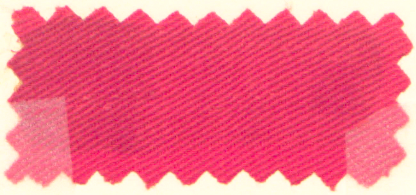
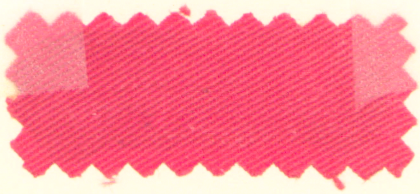
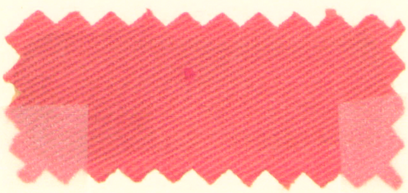
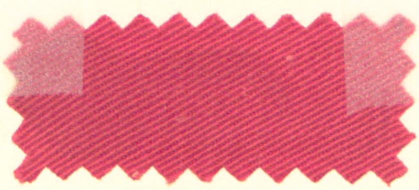
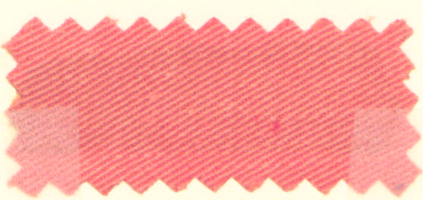
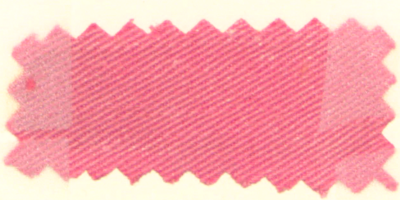
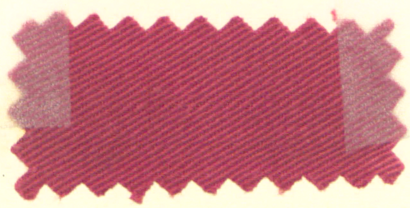
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
57	5	6	FAST SCARLET 2G BASE with NAPHTHOL AS-TMA	
58	5	7-6	FAST SCARLET 2G BASE with NAPHTHOL AS-ITR	
59	5	7	FAST SCARLET 2G BASE with NAPHTHOL AS-BG	
60	5	6	FAST SCARLET 2G BASE with NAPHTHOL AS-DEA	
61	5	5	FAST ORANGE GR BASE with NAPHTHOL AS	
62	5	6-5	FAST ORANGE GR BASE with NAPHTHOL AS-TMA	
63	5	7-6	FAST ORANGE GR BASE with NAPHTHOL AS-ITR	

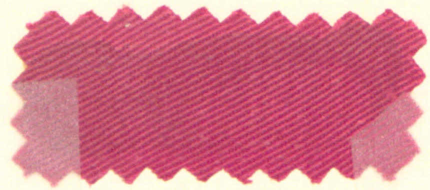
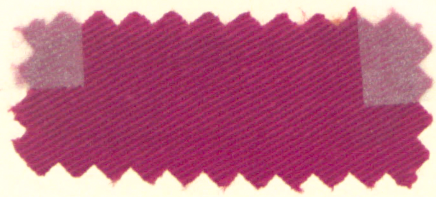
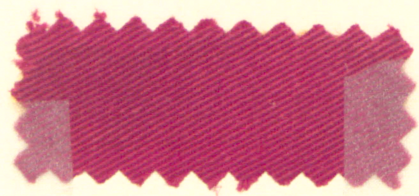
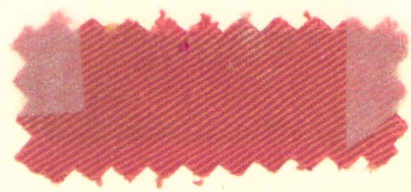
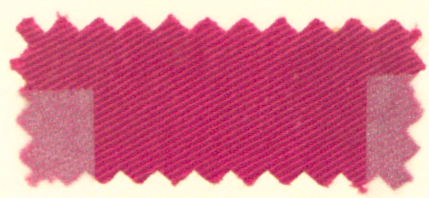
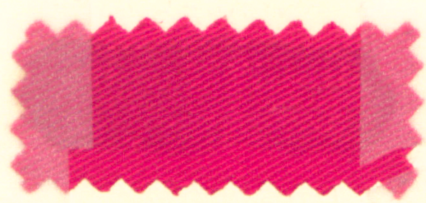
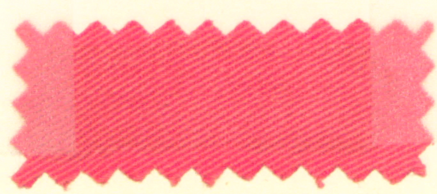
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	LIGHTFASTNESS Card No.	LIGHTFASTNESS Rating
64		FAST ORANGE R BASE with NAPHTHOL AS-OL	5	5
65		FAST ORANGE R BASE with NAPHTHOL AS-RL	5	5
66		FAST ORANGE R BASE with NAPHTHOL AS-TMA	6	5-4
67		FAST ORANGE R BASE with NAPHTHOL AS-ITR	6	7-6
68		FAST RED 2G BASE with NAPHTHOL AS	6	6-5
69		FAST RED 2G BASE with NAPHTHOL AS-TMA	6	6-5
70		FAST RED 2G BASE with NAPHTHOL AS-ITR	6	7-6

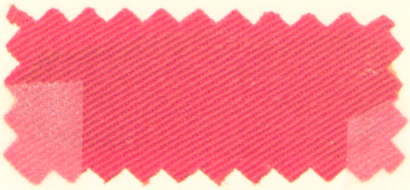
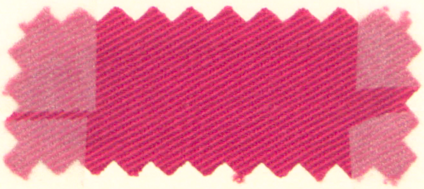
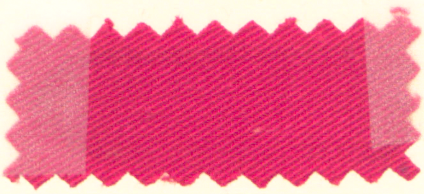
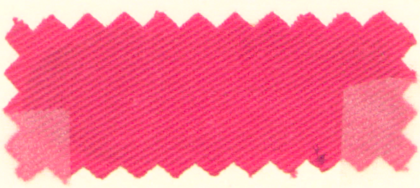
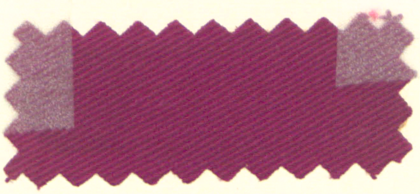
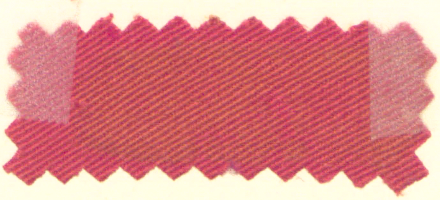
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
71	6	6	FAST RED G BASE with NAPHTHOL AS	
72	6	6	FAST RED G BASE with NAPHTHOL AS-OL	
73	6	7-6	FAST RED G BASE with NAPHTHOL AS-RL	
74	6	6	FAST RED G BASE with NAPHTHOL AS-TMA	
75	6	7-6	FAST RED G BASE with NAPHTHOL AS-ITR	
76	6	5-4	FAST SCARLET G BASE with NAPHTHOL AS-OL	
77	6	5-4	FAST SCARLET G BASE with NAPHTHOL AS-RL	

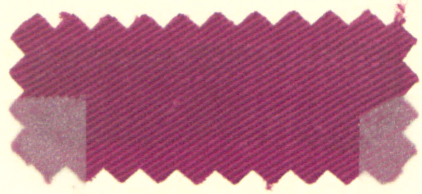
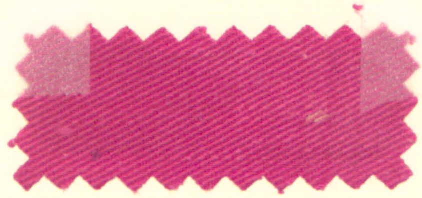
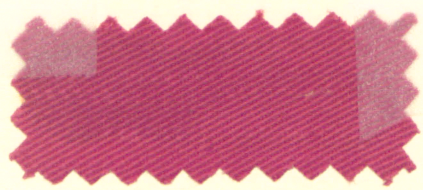
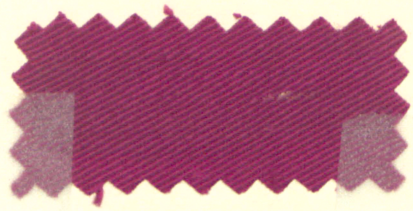
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
78		FAST SCARLET G BASE with NAPHTHOL AS-TMA	6	5-4
79		FAST SCARLET G BASE with NAPHTHOL AS-ITR	7	5-4
80		FAST SCARLET G BASE with NAPHTHOL AS-BG	7	5-4
81		FAST SCARLET G BASE with NAPHTHOL AS-DEA	7	4-3
82		FAST BORDEAUX GPR BASE with NAPHTHOL AS-OL	7	7-6
83		FAST BORDEAUX GPR BASE with NAPHTHOL AS-RL	7	6
84		FAST BORDEAUX GPR BASE with NAPHTHOL AS-TMA	7	5-4

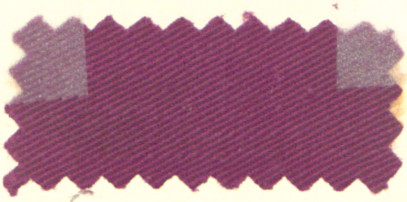
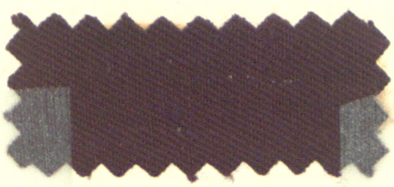
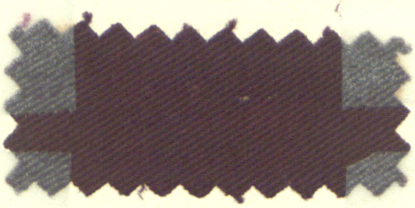
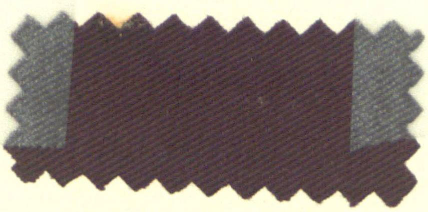
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
85	7	6-5	FAST BORDEAUX GPR BASE with NAPHTHOL AS-ITR	
86	7	5-4	FAST RED B BASE with NAPHTHOL AS	
87	7	5	FAST RED B BASE with NAPHTHOL AS-BO	
88	7	5-4	FAST RED B BASE with NAPHTHOL AS-TMA	
89	7	5-4	FAST RED B BASE with NAPHTHOL AS-ITR	
90	7	5	FAST GARNET B BASE with NAPHTHOL AS-OL	
91	7	6-5	FAST GARNET B BASE with NAPHTHOL AS-RL	

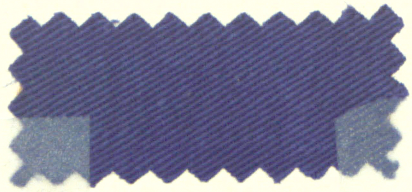
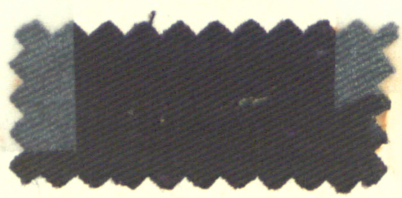
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
92		FAST GARNET B BASE with NAPHTHOL AS-TMA	8	5-4
93		FAST GARNET B BASE with NAPHTHOL AS-ITR	8	6-5
94		FAST BLUE B BASE with NAPHTHOL AS	8	4
95		FAST BLUE B BASE with NAPHTHOL AS-OL	8	4
96		FAST BLUE B BASE with NAPHTHOL AS-RL	8	5-4
97		FAST BLUE B BASE with NAPHTHOL AS-TMA	8	4.3
98		FAST BLUE B BASE with NAPHTHOL AS-ITR	8	4.3

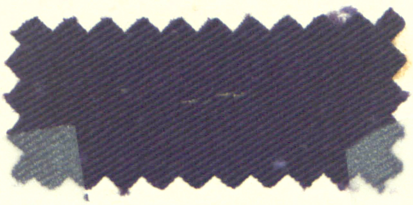
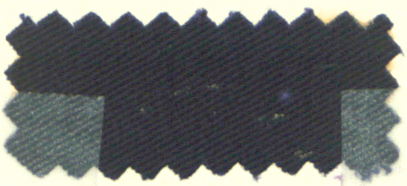
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
99	8	5-4	FAST BLUE SALT BBN with NAPHTHOL AS	
100	8	6	FAST BLUE SALT BBN with NAPHTHOL AS-OL	
101	8	5-4	FAST BLUE SALT BBN with NAPHTHOL AS-RL	
102	8	6-5	FAST BLUE SALT BBN with NAPHTHOL AS-TMA	
103	8	6-5	FAST BLUE SALT BBN with NAPHTHOL AS-ITR	
104	8	5-4	VARIAMINE BLUE SALT RT with NAPHTHOL AS	
105	9	7-6	VARIAMINE BLUE SALT RT with NAPHTHOL AS-OL	

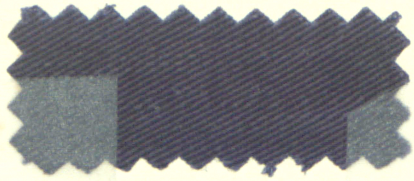
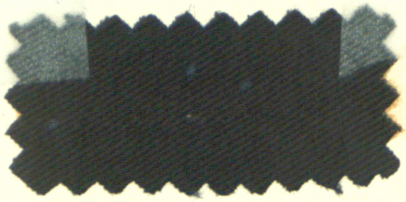
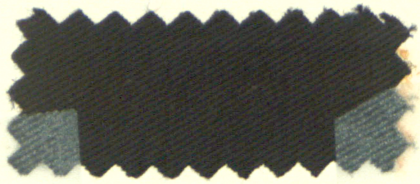
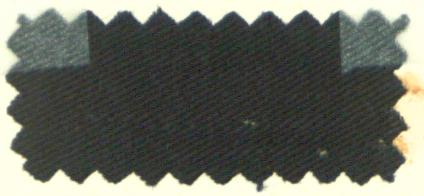
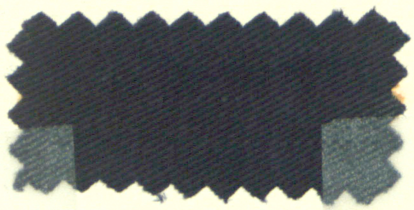
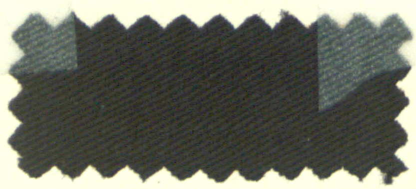
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	LIGHTFASTNESS- Card No.	Rating
106		VARIAMINE BLUE SALT RT with NAPHTHOL AS-RL	9	5-4
107		VARIAMINE BLUE SALT RT with NAPHTHOL AS-TMA	9	4-3
108		VARIAMINE BLUE SALT RT with NAPHTHOL AS-ITR	9	6-5
109		VARIAMINE BLUE SALT BD with NAPHTHOL AS	9	5-4
110		VARIAMINE BLUE SALT BD with NAPHTHOL AS-TR	9	6-5
111		VARIAMINE BLUE SALT BD with NAPHTHOL AS-OL	9	6-5
112		VARIAMINE BLUE SALT BD with NAPHTHOL AS-RL	9	6-5

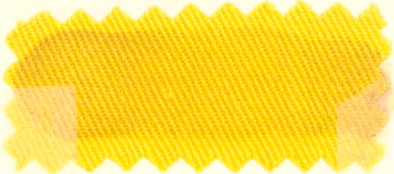
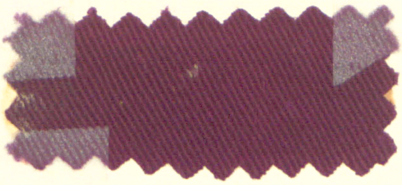
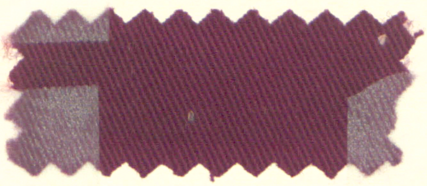
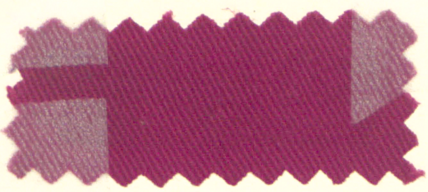
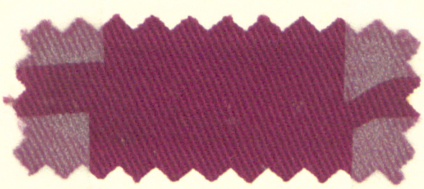
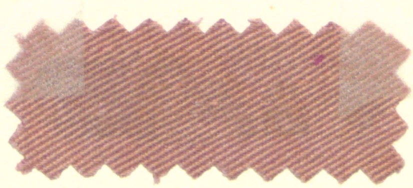
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
113	9	4-3	VARIAMINE BLUE SALT BD with NAPHTHOL AS-TMA	
114	9	5-4	VARIAMINE BLUE SALT BD with NAPHTHOL AS-ITR	
115	9	7-6	FAST BLACK B BASE with NAPHTHOL AS-SW	
116	9	7-6	FAST BLACK B BASE with NAPHTHOL AS-OL	
117	9	7-6	FAST BLACK B BASE with NAPHTHOL AS-RL	
118	10	5-4	FAST BLACK B BASE with NAPHTHOL AS-TMA	
119	10	7	FAST BLACK B BASE with NAPHTHOL AS-ITR	

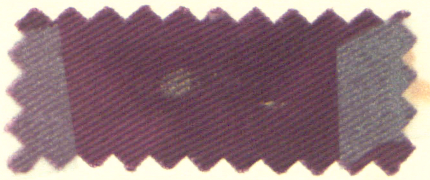
See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	SHADE	CONSTITUTION	-LIGHTFASTNESS- Card No.	Rating
120		DIMETHOXY BENZOYL-AMINO ANILINE with NAPHTHOL AS-G	11	4-3
121		DIMETHOXY BENZOYL-AMINO ANILINE with NAPHTHOL AS	11	4-3
122		DIMETHOXY BENZOYL-AMINO ANILINE with NAPHTHOL AS-D	11	4-3
123		DIMETHOXY BENZOYL-AMINO ANILINE with NAPHTHOL AS-OL	11	4-3
124		DIMETHOXY BENZOYL-AMINO ANILINE with NAPHTHOL AS-BG	11	4-3
125		DIMETHOXY BENZOYL-AMINO ANILINE with NAPHTHOL AS-ITR	11	4-3
126		TRIMETHOXY AMINO AZOBENZENE with NAPHTHOL AS	11	4-3

See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.

ICE COLORS FROM B O N ARYLIDES

DYE NO.	-LIGHTFASTNESS- Card No.	Rating	CONSTITUTION	SHADE
127	11	4.3	TRIMETHOXY AMINO AZOBENZENE with NAPHTHOL AS-OL	
128	11	4.3	TRIMETHOXY AMINO AZOBENZENE with NAPHTHOL AS-BG	
129	11	4.3	TRIMETHOXY AMINO AZOBENZENE with NAPHTHOL AS-ITR	

See tables in experimental part for constitution of naphthols and bases, and concentrations of padding and diazo solutions.