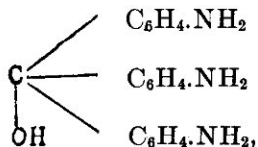


A METHOD FOR MAKING METHYL VIOLET.—BY HENRY JERMAIN MAUDE CREIGHTON, DR. SC., ASSISTANT PROFESSOR OF CHEMISTRY IN SWARTHMORE COLLEGE, SWARTHMORE, Pa., U. S. A.

(Read 12 May, 1919)

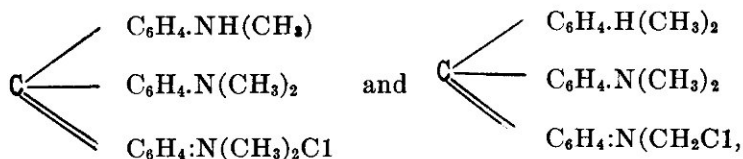
In the year 1860, C. Lauth began to study the action on mono- and dimethylaniline of those oxidizing agents which produce rosaniline, and as a result of his efforts a beautiful violet dye, now known as methyl violet in contradistinction to Hofmann's violet, was placed on the market in 1866. The discovery and preparation of this dye represent a logical step forward from the manufacture of magenta (homorosaniline chloride), even though the processes by which methyl violet is made at the present time bear no relation to any of those by which the latter is prepared. The popular misnomer "aniline dye" may justly be applied to methyl violet, for it is one of the few synthetic dyestuffs which can be traced back to aniline as a starting point.

The name methyl violet is used to designate a number of triphenylmethane dyestuffs which are derived from the parent substance *para*-rosaniline,



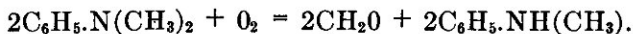
by partial or complete substitution of the hydrogen atoms of the amino groups by alkyl groups. Since substitution in a compound by batho-chromic groups (methyl, ethyl, hydroxymethyl, etc.) is attended by a displacement of the absorption bands towards the red end of the spectrum, causing the color of the substance to pass successively into the yellow, orange, red, purple and violet, the substitution in *para*-rosaniline by alkyl groups caused the red color of the former to change to violet, the shade of the violet color of the derived substance approximating more closely to the blue or red

according as the number of alkyl groups is greater or less. The red or blue shades of the various alkyl substitution products of para-rosaniline are usually denoted by affixing to the name methyl violet the letters R, 2R, 3R, B, 2B, 3B, etc. Thus Hofmann's violet, which is a mixture of the lowest substitution products of para-rosaniline, gives shades corresponding to the letters R, 2R and 3R. On the other hand methyl violet, as prepared in the manner described below, is essentially a mixture of the hydrochlorides of penta- and hexamethyl-rosaniline,

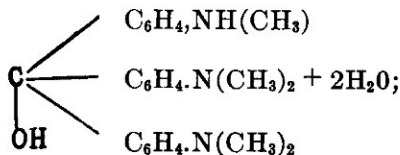
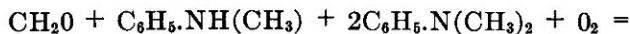


and accordingly gives bluer shades than Hofmann's violet, which correspond to the letters B and 2B. A preponderance of the penta-compound gives a methyl violet B, while an increase in the proportion of the hexa-derivative produces a methyl violet 2B.

Methyl violet B or 2B is formed by the action of a number of oxidizing agents on dimethylaniline. The first step in its formation is the production of formaldehyde and monomethylaniline:

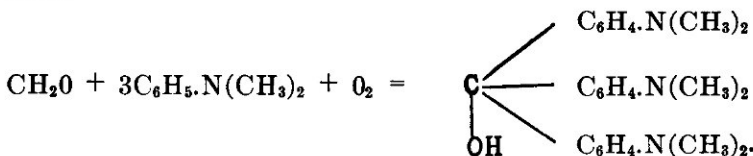


Part of the formaldehyde, which supplies the so-called methane carbon, then combines with one molecule of monomethylaniline, two molecules of dimethylaniline and one molecule of oxygen to form the penta-carbinol base:



while part of it combines with three molecules of dimethyl-

aniline and one molecule of oxygen to form the hexa-carbinol base:



Treatment with hydrochloric acid converts these carbinol bases into the corresponding hydrochlorides.

In the manufacture of methyl violet at the present time, copper sulphate is employed as the oxidizing agent. This salt reacts with some of the sodium chloride present in the reaction mass (melt) to form cupric chloride, and this is reduced to cuprous chloride. As this latter compound is easily reoxidized to the cupric salt, *in situ*, by atmospheric oxygen, the melt was formerly rendered porous by the admixture of a large quantity of sand so that the air might have ready access. At the present time the use of sand has been entirely replaced by common salt, as this can be easily removed by dissolution immediately after oxidation, thus considerably decreasing the bulk of the product to be worked with.

The following method for the manufacture of methyl violet has been developed by the writer and gives very good results:

A quantity of finely-ground copper sulphate, corresponding to 12 kilograms of the hydrated salt, is intimately mixed with 190 kilograms of dried sodium chloride. To this mixture, under constant stirring, is added 8 kilograms of phenol dissolved in one liter of water, and this is followed by the gradual addition of 20 kilograms of dimethylaniline. The melt is transferred to a closed iron vessel equipped with a stirring and mixing device, where it is continuously stirred at a temperature of 57-60°C. until a sample when squeezed in the hand forms a ball which does not fall apart. This usually requires about eight hours.

The reaction liberates a considerable amount of heat. This may be increased by dehydrating the copper sulphate prior to mixing with the salt. By employing the dehydrated salt, or suitable proportions of hydrated and dehydrated

salt, the amount of external heat required to maintain the melt at the proper temperature may be decreased, thus effecting a saving in fuel.

When oxidation is complete, the melt is gradually added to a large wooden vat containing 1000 liters of boiling water, in which are dissolved 13 kilograms of slaked lime. The liquid is boiled, by blowing in high pressure steam, until all the lumps disappear. The insoluble double salt of the color base and cuprous chloride is allowed to settle and the supernatant liquid runs off. This liquid contains most of the salt and the phenol in the form of calcium phenate. The double salt of the color base and cuprous chloride is now decomposed with sodium sulphide, which converts the latter into copper sulphide. To accomplish this 1000 liters of water are run into the vat, the temperature brought to 70°C., and 3.3 kilograms of sodium sulphide dissolved in a small quantity of water slowly added while the liquid is stirred continuously. At the end of one-half hour the temperature is raised to 100°C. and the liquid boiled for five or six hours. The color base and the copper sulphide are then allowed to settle, the supernatant liquid run off, and the residue washed twice with 1000 liters of water.

In order to separate the color base from the copper sulphide, 1000 liters of water are run into the vat, the mixture brought to boiling, 15 kilograms of sulphuric acid gradually added, and boiling continued for two hours. During this treatment the color base dissolves, forming a deep violet solution, practically all of the copper sulphide remaining undissolved. After the solid material settles, the solution of dye is run off into a second vat, at a lower level, and the residue in the first vat is again extracted with sulphuric acid. The resulting solution of dye is combined with that in the second vat. To the combined liquids sufficient sodium hydroxide is added to almost neutralize the acid. The dye is now salted out by the addition of sodium chloride, and on cooling it solidifies to a lustrous green resinous mass. As this dye contains a small quantity of the insoluble copper compound, it is redissolved in 750 liters of boiling water. The dye solution is passed through a filter into a third vat where, on salting out, a particularly pure methyl violet is obtained. The insoluble residue remaining in the second

vat and in the filter is added to the first vat, where it is again treated with sodium sulphate with the next melt.

The method that has been described has been operated under the supervision of the writer's assistants, Messrs. K. R. Brown, C. D. Pratt and J. E. Allen, and has given yields of 75-85 per cent. of methyl violet. The color of the dye produced had a 2B shade.

Swarthmore College,
Swarthmore, Pa.,
April 9th, 1919.