CCXXXVIII.—*Theory of Dyeing: the Colour and Molecular State of Picric Acid.*

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PICRIC acid in the anhydrous state is probably colourless. It is nearly so under conditions of long exposure to the action of dehydrating agents acting through a vacuum.

In the colourless condition it has been regarded as having an *o*- or *p*-quinonoid constitution.

An investigation into variations in the conditions of formation of the colourless variety in the presence of fibre colloids (Dreaper and Stokes, *J. Soc. Dyers*, 1909, **25**, 10) with the results now recorded has led to this consideration of the possible molecular structure in relation to its behaviour under these conditions. It may be mentioned that Vignon (*Rev. Gen. Mat. Col.*, 1909, **13**, 156) has compared the dyeing properties of picric acid with the electrical conductivity of its solutions, and that Dreaper and Davis (*Internat. Congr. Appl. Chem.*, 1909, Sect. IVb, 7) have confirmed that picric acid in aqueous solution is not subject to de-solution when passing through a sand column. Walker and Appleyard (*Trans.*, 1896, **69**, 1334) have also discussed the dyeing action of picric acid on silk, and have shown that the law of the distribution of picric acid at 60° is:

$$s/\sqrt[2.7]{w} = 35.5.$$

It has been assumed for the purpose in hand that the condition of attraction or strain exhibited by atoms for one another, and the attraction observed as between molecule and molecule, is identical, and in both cases can be referred back to the attraction of atoms acting at varying distances; thus, molecular attraction is regarded as primarily due to the attraction of the atoms in one molecule for those in the surrounding molecules within the active sphere of influence, and not to the attraction of molecule for molecule (see *Chem. News*, 1905, **92**, 299; *Proc. Faraday Soc.*, 1910, 31). It is further assumed that the sum of the primary attraction (as between atom and atom in the same molecule) and the secondary attraction (as between an atom in one molecule and those in others) is at its maximum a constant. The secondary attraction under these conditions would increase as the primary attraction decreases.

It is assumed for the moment that the picric acid molecule is actually in association with *x* molecules of water (dihydrone or hydronol) in the coloured type. It is difficult to escape this conclu-

sion if this is the cause of a change in molecular structure, and the following facts must then be considered.

The colour intensity apparently increases to a maximum before actual solution takes place, and the ratio of the assembled molecules of water to those of picric acid has increased to a degree where such a change in physical state is involved. Change of colour is therefore not connected in this case with actual solution, unless it is assumed that the one type of picric acid is in solution in the other.

Assuming, therefore, that an association of the order suggested exists, and that this is as between atom and atom, although apparently expressed by outward molecular attraction, and, further, that this attraction under certain conditions may be localised, it will then involve either the $\text{H}\cdot$, $\text{NO}_2\cdot$, $\text{OH}\cdot$, or O groups. Any secondary association may then be represented as follows:

It will be observed that the last combination is the only one known to exist in the free state. It is suggested that this possible condition correspondingly induces secondary attraction of a localised order, which may then take place as between such units. The assumption that the sum of the primary and secondary attractions has a maximum value has in this respect a definite significance. The effect of such localisation will be to reduce the general attraction (as between molecule and molecule), the former taking its place. If ordinary attraction as between atom and atom be represented by . localised attraction may be written as . . and general attraction as influencing molecule and molecule as . . .

It is seen that association of this localised order is only possible with the quinone or an equivalent type. An equilibrium condition between the picric acid and water molecules may be set up, under which there is a tendency for the colourless type to be replaced by the coloured one.

It is then assumed that the secondary attraction as between the $(\text{OH}_2)_x$ molecules and the oxygen atom is sufficient to displace the equilibrium existing between the two types in the direction indicated, and to suppress the ordinary type in favour of the coloured one. The above attraction between the $(\text{OH}_2)_x$ molecules and the oxygen atom would under these conditions partly replace that of the $\cdot\text{H}$ atom, and the latter would under these conditions of strain migrate to the neighbouring NO_2 -group, with the formation of a compound of quinonoid type.

If this localised affinity exists, the oxygen atom, from its isolated position and the fact that it is in combination with a monatomic hydrogen atom, might favour such an action. Be this as it may,

the above consideration affords a possible explanation of the cause of the action observed if the quinone type is actually formed, and if this action is accepted as the cause of the colour change.

The solvent action of toluene when it replaces water is of a different order. In this case the colourless type is present to the virtual exclusion of the coloured one. The yellow variety dissolves to a colourless solution. It must be assumed in this case that association is of a more general order, and non-localised. There is no side-group which can associate with the solvent molecules in the manner suggested in the case of water.

By mass action the water associated with the picric acid in solution is replaced by toluene, and the colourless type is once more in stable equilibrium with the solvent.

Solutions of picric acid in water and toluene respectively may then be represented by the following types:

In the former case water is represented as being associated locally (.) as well as generally (. . .). The secondary association may naturally be modified by certain internal groupings, possible close-packing of the atoms, etc., with their attendant condition of strain.

It must be considered whether there is not a more convenient method of considering the change which takes place from one type to the other. If the hydrogen atom migrates, it may well carry with it its bond of attraction, and the change may then be indicated in the following manner. As the mechanism of change in intra-molecular condition is apparently in this case a simple one, the change may not necessarily entail the production of the quinone type to allow of salt formation, etc.

The colour may have its origin in a change of type as indicated below in the intermediate type, which, if unstable, may then pass into the quinone type:

x may or may not equal y in this case.

Alternate methods of association may suggest themselves for comparison with the above. In the quinone type, association may be as between the side-groups generally and the water molecules,

owing to position, but this does not seem to be the case in a solution in toluene; or association may take place as between the $(\text{OH}_2)_x \dots$ group and the other oxygen atom, as follows:

It will be remembered that the loss of colour has also been ascribed to the suppression of free hydrogen ions. In that case of association the presence of free or migrating ions is not impossible, owing to the reduction in the primary bond and an interchange of atoms from one molecule to the other under this condition. This action might be represented graphically in the following manner:

Association may therefore be of a general order, except where conditions are present which supply a tendency to form separate groups or independent units, and then association may be localised in the manner suggested. In the latter case the modification in the general state of equilibrium may be sufficient to disturb the general system and induce certain changes, as in the case of water and picric acid.

The salts of picric acid are coloured, and may be regarded as being of the quinone type. The association as between picric acid and animal and vegetable fibre respectively, where in the former case the change from the coloured type to the colourless does not take place in a vacuum, may possibly be expressed in the following terms:

The colour change can take place in (3), but not in (2), and in the case of silk dyed at 15° , where a certain loss of colour is observed in a vacuum, the change observed may take place in (1), which may be present at such low temperatures of dyeing. This agrees with the experimental results.

EXPERIMENTAL.

The rate of change from the coloured to the colourless type of picric acid when present on the fibres under the action of certain dehydrating agents acting in a vacuum has thus been shown to be of a definite order (Dreaper and Stokes). On vegetable fibres the change is facilitated, whilst on animal fibres it is entirely prevented.

The comparative action of water and toluene on picric acid present within the fibre area has now been examined, it being known that picric acid dissolves in toluene, giving an almost colourless solution.

Silk (fibroin) was dyed at 95° in the usual manner from an aqueous solution containing 3 per cent. of picric acid of the weight of silk taken, the ratio of silk to solution being 1:200. On immersion in toluene no change in colour or any appreciable re-solution of the dyestuff in the solvent could be observed. This result agrees with that previously obtained with the silk fibre substance and picric acid in a vacuum where this inter-relation prevents any change in type taking place under conditions on which picric acid itself loses colour. As the yellow variety of picric acid passes immediately into a colourless state on solution in toluene, the union between the picric acid and silk fibre-substance evidently prevents this normal change to the colourless type.

When cotton replaces silk, the results are of a different order from those obtained with dehydrating agents. When this fibre is coloured or stained with picric acid from a saturated aqueous solution of the latter, the picric acid is held so loosely that resolution in water is immediate, the colour being removed on agitation with water (ratio of fibre to water=1:1000) in twenty seconds. On the other hand, practically no loss occurred from the fibre area after thirty minutes' extraction with toluene at 17° , nor could any material change from the coloured to the colourless type be observed. The yellow variety is therefore stable (and insoluble) under the conditions indicated.

Following this result, it was observed that cotton may under certain conditions absorb picric acid and dye the fibre an intense yellow shade from its colourless toluene solution. This action seems to depend on the presence of oxycellulose. Under these conditions silk remains colourless, so that the dyeing properties of picric acid

in toluene as judged by colour indications are the reverse of those exhibited in aqueous solution, where the yellow variety is present within the silk area, and the cotton, except in a solution of high concentration, remains white, and absorbs no picric acid.

The silk remained colourless on evaporating the toluene, and the cotton still exhibited a full and brilliant shade of yellow. Samples treated in this manner were subjected to the action of water vapour at 100° and 15° respectively. The silk gradually assumed a yellow shade, and the cotton also visibly deepened in shade; but in water under the conditions before mentioned, the cotton still lost all its colour in twenty seconds; the silk lost about 60 per cent.

A development in shade was noticed on exposure to a damp atmosphere in the place of steam, but the rate of change from the colourless to the coloured type within the fibre area was not so rapid or so complete as after the action of the dehydrating agents, as previously recorded.

The influence of the presence of moisture in the cotton on the result obtained was next investigated. A sample was dried at 110° for one hour, and another was treated with steam before immersion in a solution of picric acid in toluene. The dried sample was much lighter in shade, and the steamed one darker. Taking the depth of shade of the ordinary cotton after treatment as 100, the dried one was represented by 70 and the steamed one by 150. After forty-eight hours' exposure of the samples so treated to the action of a saturated atmosphere at 15° , all the samples developed in colour to a standard shade, indicating that the depth of colour assumed by the fibre at the time of contact is no guide to the amount of picric acid actually absorbed, but only of the proportion of the moisture present in the cotton fibre area.

Cotton containing 6—8 per cent. of natural moisture developed a yellow shade under these conditions, whilst silk containing 10—12 per cent. of natural moisture remained colourless. The nature of the condition under which the water is present within the cotton and silk fibre area is therefore a determining factor. It is possible that in the case of silk the toluene may not penetrate into the silk substance, and therefore no absorption of picric acid can take place; but this does not agree with some of the results obtained. It may be noted that the former assumption has been held to explain certain obscure reactions which occur in the practical manipulation of these fibres.

A sample of silk was immersed in water, and all superfluous moisture carefully removed under pressure in a dry cloth. On subsequent immersion in the toluene solution the silk at once assumed a fairly deep shade of yellow, indicating that the yellow

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variety can exist under these conditions in the silk fibre. The action was a non-reversible one, for after drying to remove interfering moisture the colour remained to its full intensity on subsequent immersion in toluene. When once the conditions in the animal fibre are present which determine the formation of the yellow variety, it is apparently more stable than the colourless one.

Sisley has noticed that in dilute solution the whole of the picric acid is present in the water in a mixture of water and toluene, and even in strong solution the ratio is still 4:1. The subsequent development of colour in the above samples containing varying amounts of moisture to a common shade does not indicate that the actual adsorption is directly caused by the presence of moisture. This condition seems to govern the ratio of change from the colourless type to the coloured one.

In the case of silk the natural resistance against change is probably due to the fact that the moisture present is in some closer relationship with the fibre colloid, and that this prevents it from reacting with, and producing the colour change with, picric acid observed in the case of cotton; but this change can take place in the presence of water, which is not so closely associated with the fibroin. When the change has taken place as in the case of a silk fibre which obviously contained "free" moisture, some further action between the silk substance and the yellow type prevents the subsequent reversion to the colourless type in the presence of toluene.

Thus, whilst "free" moisture must be present in order that the yellow variety may exist in the silk fibre area, yet there is an adsorption of the colourless variety from toluene in its absence. This follows from the fact that on subsequent steaming the colourless silk develops a yellow shade, even after a final treatment with toluene to remove any surface picric acid which in itself might account for this action.

The relationship which exists between an animal fibre-substance and picric acid which prevents or inhibits the loss of colour on exposure to the dehydrating agents, and resists resolution and a return to the colourless type in the presence of toluene, is apparently different in the case of vegetable fibres. The action of dehydrating agents in this case causes the cotton to lose its colour, but does not do this in the presence of toluene, so that these reactions indicate in further detail the nature of the affinity which apparently exists between the fibre and the picric acid.

It may be argued that an affinity exists between the picric acid and cotton fibre-substance which prevents the normal change to the colourless type taking place in the presence of toluene; so that

whilst the picric acid is easily removed by water from the fibre area, this action cannot take place in the case of toluene. This agrees with the assumption that the yellow variety is insoluble as such in toluene, and that the latter cannot bring about a change of type in the presence of the cotton fibre-substance. The yellow variety being soluble in water is easily removed. As picric acid will dye cotton from a toluene solution, it may be argued that this suppression of colour change is not due to any want of penetration of the solvent into the fibre.

The results obtained may be summarised in the following manner :

Nature of Fibre.	Action of dehydrating agents acting through a vacuum.	Action of toluene on picric acid within the fibre area.
Silk	No loss in colour	No loss in colour
Wool	" "	" "
Cotton	Loss of colour in excess of that in acid itself	" "