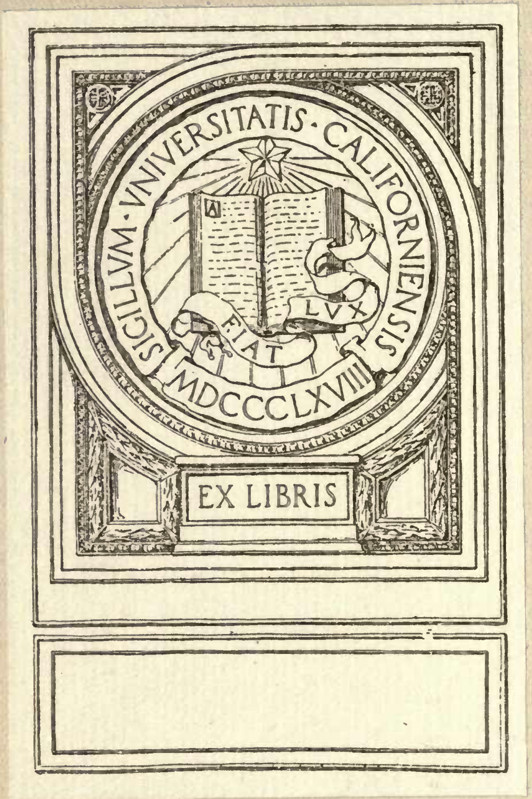

THE CHEMISTRY AND PHYSICS
OF
DYEING

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BEING AN ACCOUNT OF THE
RELATIONS BETWEEN FIBRES AND DYES,
THE FORMATION OF LAKES, AND THE
GENERAL REACTIONS OF COLLOIDS, AND
THEIR SOLUTION STATE

BY

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Illustrated by Curves and Numerous
Tabulated Results

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PREFACE

In the present volume an attempt is made to collect and classify the work which has been brought forward to explain the action of dyeing, mordanting and lake formation.

The general text-books on dyeing devote little space to this particular side of the question. They deal with the operations of the dye-house, rather than with the principles which seem to govern the actual practice of this branch of industry.

It is advisable that the modern dyer should have some knowledge of the general reactions, which give rise to the results obtained in the many processes, involved in the dyeing, and bleaching of textile fibres. Without some such knowledge, it is difficult to appreciate their nature; or be in a position to control their working in a systematic manner.

To obtain this under present conditions, it is necessary to make a more, or less, tedious search over the scientific and technical journals of the last thirty years.

This same difficulty presents itself to the student, who wishes to engage in research on this interesting, but little understood subject.

It is, perhaps, equally difficult for the dyer to obtain information of those branches of physical science, which will possibly give an explanation of many of the mordanting and dyeing operations met with in daily practice.

With the extension of our knowledge of general physics, and the breaking down of the artificial barriers set up during the nineteenth century between the different branches of experimental science, has come a wider outlook. The subject before us forms an interesting chapter in the evolution of theoretical speculation in its application to the principles of a well-known, but little understood industrial process.

From the very nature and complexity of the subject, it is more than likely, that any further advance in our knowledge will come from within the industry itself. With the increasing number of chemists who are devoting their time to this subject, and gradually displacing the "rule of thumb" methods of the past, this does not appear to be improbable.

At the present time, the art of dyeing may be said to be in advance of the science of the subject. The first step towards restoring the balance, is to take a general survey of the work done in the past, by the many investigators who have given this matter their attention. The foundation on which we rest our present ideas of the nature of the dyeing phenomena met with in our dye-houses, and finishing factories, must be realised before any further advance is possible. The subject has been treated from this point of view. The object of this book is to give the practical dyer, and student, a collected record of the work done in the past, so that it may be available for reference.

It is only by referring back the observed phenomena in dyeing to the first principles of chemistry and physics, that we can expect to advance beyond the present state of uncertainty as to the nature of the actions involved.

The need for further research along systematic lines is urgent. Much might be done in the dyeing departments of our technical institutions, if a definite scheme of research could be devised, and carried out.

Then, perhaps, the process of dyeing with all that it entails, will take its place in the general scheme of physical science.

A study of the name index indicates how little of this work has been done in England, and the steps which are necessary in the future, if this country is to hold its own in the dyeing industry.

The dyer must watch other things besides his dye-pots, and his tinted yarns. He must know something of the general reactions of colloids, as typical of those which may possibly take place in the substance of the materials he has to prepare, and dye. It is important too, that he should have some knowledge of the general principles which seem to govern solution, and the action of temperature, &c., on the dye liquors, and fibres.

This book is therefore written to supply the practical man with this knowledge. It is also hoped that it may induce the student to embark on original work, and by supplying him with an outline of what has been already done on the subject, indicate new lines on which further work may be undertaken with advantage. A close study of this subject on systematic lines, and in its wider aspect, cannot fail to lead to important results.

It is difficult, under present conditions, to entirely do away with the divisions, which still exist in connection with the study of dyeing phenomena. While sympathising with those who are ready to take this step, the author feels that had this book been written on these lines, it would have been less useful to the majority of readers.

It is quite possible for the student to steer a middle course, and, keeping for convenience the old divisions before him, to remember that the general scheme of research is an artificial one at best, and that the recognised divisions are of an arbitrary nature. This is being demonstrated daily. All that the student in dyeing, or the practical dyer, needs to remember is, that these divisions are upheld on the grounds of general convenience.

To the general student of chemistry it is doubtful whether there is at the present time a more fruitful subject of research than that of dyeing. It is hoped that the publication of the chief work which has been done on the subject in the past in the present form will tend to increase the interest taken in this subject, and at the same time raise the standard of the work done.

Wherever possible, references have been given to the original communications in which the recorded facts have first appeared, in order that fuller knowledge may be obtained for special purposes.

The facts mentioned under their different headings are also, as far as possible, put forward in their historical sequence.

In this way the gradual development of the subject under review may be followed from the earliest investigations, and speculations, of Hellot in the year 1734 to the present time; and an insight into the probable nature of dyeing obtained.

This can hardly fail to be of interest to the dyer, whose aim should be, first of all, to understand the principles which control the many and varied operations of dyeing, and by this means obtain more regular and satisfactory results in the practice of his art.

The author wishes to express his thanks to Mr. W. A. Davis, B.Sc., for his help in the revision of proofs and for his valuable suggestions.

THE AUTHOR.

September 15, 1906.

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CHEMISTRY AND PHYSICS OF DYEING

CHAPTER I

HISTORICAL INTRODUCTION

THE art of dyeing has been practised for long ages. Its origin is lost in antiquity. There is distinct evidence that operations of this nature were carried on in Persia, Egypt, the East Indies, and Syria in early days. The Tyrians excelled in the production of the celebrated purple of Tyre, and seem to have made its manufacture one of their chief occupations. This colour was noted for its richness and durable qualities. It is believed that the method of dyeing this colour was invented about the year 1500 B.C. Wool dyed in this way sold in Rome at a price equivalent to £30 per pound.

The purple of Tyre seemed to vary in its colour. Pliny mentioned that the shade varied from a faint scarlet to the red of coagulated bullock's blood.

The origin of the shell fish from which the colour was developed seemed to determine the shade. The Atlantic variety gave the darkest colours, while those obtained off the Phœnician shore yielded the scarlet shades. The dye prepared from these varieties of shell fish was probably developed by some process of oxidation; the exact nature of the operation being unknown.

The secret of the production of this colour was carefully guarded, and in this way a virtual monopoly was established.

It was not until the fourteenth century that the art of dyeing flourished in Europe. Florence was one of the headquarters of this industry.

An inferior cochineal, or kermes, was collected by the Arabs about this period.

This same product was known to the Greeks and Romans under the name coccus. It is interesting to note that between the ninth and fourteenth centuries, the rural serfs were obliged to deliver to the convents a certain quantity of this dye annually. A great deal of this German kermes was consumed in Venice for the dyeing of scarlet.

Pliny ("Hist. Nat." lib. xxxv. cap. 11) draws attention also to the extraordinary method of dyeing linen in Egypt. They clearly developed the colour on mordants in this case.

A great change came about in the dyeing industry with the discovery of America. With the trading which sprung up between the two continents many very valuable dyewoods were introduced to Europe. Among these may be mentioned cochineal, logwood and annotto.

About this time also Oricelli discovered the action of ammoniacal liquors on certain lichens with the production of coloured bodies which might be used for dyeing organic fibres. These have only given way before the aniline colours. A great development took place about the year 1650, when tin salts were introduced as a mordant in the place of alum; and with this introduction we have the production of the first really brilliant colours on fibres. As the result of the discovery, a large dye-house was established at Bow. Cochineal was dyed on this mordant with great success, and the colours produced in this district were justly celebrated for their purity and beauty.

In the year 1548 the first text-book on dyeing appeared. The production and publication of this book had a great effect on the art in Germany, France and England. The dyeing operations in these countries were greatly extended as a result; and the almost complete monopoly which had existed for nearly a century or more in Italy was gradually broken down by this natural extension of the industry. The year 1667 was a most important one for England. A Fleming coming to England brought with him the art of dyeing wool in a state of great perfection. Since that date it has been maintained at a high level in this country, and sets a standard to the world.

With this increased activity came the publication of several works on the subject. This greatly widened the interest taken in this important and lucrative branch of industry.

The dyeing with woad was of importance in this country, and the introduction of indigo, with its superior colours on wool, created a scare amongst those interested in the woad industry. Severe measures were taken by the government to keep this product out of the country. It was not until the reign of Charles II. that its use was permitted in the English dyehouse.

As might be expected it gradually replaced the native woad, until to-day the latter is only used in limited quantities for the "indigo-woad" bath in some special dyeing districts.

In the eighteenth century the art made great progress. About this time madder was used in large quantities and quercitron introduced. Mordants were also manufactured in a purer state, with the natural result that the colours were correspondingly brighter in shade and of increased beauty.

Mineral colours were also introduced and used in the colouring of fibres, being precipitated in their substance. In the year 1734, Hellot published his celebrated book on wool-dyeing, and this again led to the natural extension of the industry. "L'art de la teinture des laines et des étoffes de laine" was a most important work, and its influence was great on the industry.

About this time, also, the value of Turkey red as dyed in India gradually impressed the European dyers with its great and almost unique value. As a result of this, the French government in 1765 caused the details of this process of dyeing to be published. To-day the seat of this industry is in Europe, although it may possibly drift back to the East again. Two other important books were published in France during this century.

Le Pileur d'Apligny in 1776 published "L'art de la teinture des fils et étoffes de coton," which has been generally recognised as marking a stage in the development of this subject.

"Les élements de l'art de la teinture," by Berthollet, published in 1791, and "La chimie appliquée aux arts," by Chaptal, in 1807, greatly added to the knowledge of dyeing.

These publications undoubtedly tended to give to France that superior position which she has so long held in the art of dyeing. Their influence is difficult to over-estimate. The list of important books published in France on this subject must also include the following:

"Leçons de chimie appliquées à la teinture," by Chevreul in 1828–1831; "Traité de chimie appliquée aux arts," in 1828–1846; "Leçons de chimie industrielle," by de Girardin, published in 1837; "Traité théorique et pratique de l'impression des tissus," by Jean Persoz (1846); "Cours élémentaire de teinture," de Vitalis (1823); "Manuel complête de teinture," Vergnaud (1832).

Another great step in dyeing as practised in Europe was taken during the early part of the eighteenth century. Calico printing in its rudimentary stage was introduced. This industry has grown to enormous proportions. This very rough sketch of the early days of dyeing brings us up to the time when dyers began to study the theoretical basis of their operations, and to trace the possible actions of dyes and fibres; and the part which they respectively played in the process of dyeing.

From these early speculations by easy stages our knowledge of this subject has gradually developed. When we look back, remembering the elementary state of scientific knowledge of those days, and the admittedly complex nature of the processes of dyeing, we cannot but give a full measure of praise to the work of the early investigators, before whose eyes the first opening out of this subject must have been of great interest.

Even to-day, with our extended knowledge, we are yet ignorant of the exact and complete causes which bring about many of the complicated and varied effects, which are classified under the comprehensive term, dyeing.

Much of the detail, at any rate, is little understood. From the simpler speculations of these investigators, and their rough experiments on pound-samples of wool, the student of to-day may derive valuable information and an insight into the early methods of dyeing.

At the present time we are passing through a transition state, and until the general ideas of molecular physics and chemistry reach a more satisfactory and sure basis, it is difficult to expect that our knowledge of the operations of dyeing can rest on a sure foundation.

It is, however, certain that if the study of dyeing be taken up in the proper spirit, the results obtained must influence on their side, either by confirmation or otherwise, many of the most important speculations in the domain of solution, and other equally important phenomena. The abnormal nature of the reactions in dyeing, and the very delicate nature of the available colour-tests, combine to present us with an effective means for further investigations into the state of matter, under favourable conditions. This point is not so generally recognised as it should be, owing, perhaps, to the intimate knowledge of the practical part of the question, which is necessary before the facts observed in the dyehouse can be given their true significance. This is only obtainable by direct contact and continued observation of the dyehouse routine. In this way, and this way only, will many abnormal conditions, and results, yield to the investigator their true significance.

In the earliest days there were the upholders of mechanical and chemical theories of dyeing. Ever since the middle of the eighteenth century, the conflict has raged round these two hypotheses, greatly to the benefit of our knowledge of dyeing. In the search after fresh evidence many new and important facts have come to light. The influence of this has been satisfactory, and has led to improvements in the processes of dyeing, and the gradual recognition of the fact that scientific methods are necessary in the dyehouse. To-day we have other possible explanations of the causes of dyeing, which, however, in their broadest terms, may still be referred back to these early and rival ones.

There is a tendency at the present time to discard such artificial barriers as divide the operations of nature into almost watertight compartments. The terms mechanical, physical, and chemical, are more and more regarded as mere phases, referring phenomena back indirectly to a common origin of matter and force.

It is not necessary for the dyer altogether to discontinue those divisions of the past, which by their very limitations have led to the necessary concentration of ideas along certain lines. The time is not yet come when we can do so with any certainty or advantage. To the present system we must at least ascribe our present position. It is doubtful if, for some time to come, any advantage would be gained by giving up these general divisions, which have proved so useful in the past. At the same time, the student must keep an open mind on this subject. There is no indication that the problem before us of indicating the true *cause* of dyeing is becoming less complex in its nature. Some new principle or factor in general physics may be applied to dyeing operations, and in this way our knowledge may be greatly extended. To-day, other theories besides those already mentioned have their upholders. Dyeing has been, for instance, associated with "solid solution," and an attempt has been made to extend this state to cover the absorption results when a dye is taken up by an organic fibre. From another point of view the dyeing effect has been ascribed to " dissociation effects."

Our increasing knowledge of the general reactions of colloids, in which class we may include the textile fibres, is modifying our views ; and the condition-reactions of these complex bodies has given rise to what is termed the " colloid " theory of dyeing.

The time has, perhaps, come when it is necessary to classify the researches of the past in this and kindred subjects, and formulate the general conclusions which have been arrived at from time to time, and examine them from the practical dyers' point of view. It is unfortunate that the majority of investigators have contented themselves with working on a qualitative rather than a quantitative basis. Little care has been taken to work with pure materials on the one hand, or under recorded conditions on the other. It is, therefore, difficult to form an estimate of the reliability of the recorded results in many cases where accuracy of detail and conditions are of the first importance.

No doubt, our further inquiries into this subject will enable us to classify more correctly the recorded results of the past than is possible at the present time.

Space has been devoted to the consideration of our present general knowledge of the properties and nature of colloids, and a short *resumé* of the work done on this subject has been included in this work. The abnormal actions of these substances in a state of solution are of great interest to the dyer.

They seem to approximate to the results obtained in the dyehouse.

For full details of the chemical constitution of the dyes used to-day, the standard text-books on this subject must be consulted. As regards the possible actions in the operations of dyeing in relation to their constitution, the matter is dealt with in this work in an elementary way.

CHAPTER II

PROPERTIES OF FIBRES AND THEIR REACTIONS

So much has been written on the properties of the fibres themselves in their physical aspect, that no great space will be devoted to this subject. This matter should, however, receive careful attention, and the standard works on the subject should be consulted.

The most important properties of the leading fibres are briefly reviewed here.

For our purpose we may fairly recognise the accepted classification of the fibres into those of animal and vegetable origin respectively.

From the present point of view, our knowledge is mainly confined to the three important fibres, silk, wool, and cotton. So far as the others are concerned, with perhaps the possible exception of jute, little work has been published. In these cases dyeing is of an empirical nature, whatever may be said of our knowledge in the first mentioned cases.

It is strange that more attention has not been given to the reactions entailed in the dyeing and mordanting of these other fibres. A systematic and regular survey of the comparative reactions of these towards dyes, &c., in relation to their physical nature, could not fail to give important results.

Cotton.—This fibre may be regarded as a long tubular compound vegetable cell. It is 1200–1500 times as long as it is broad. The outer sheath is considered to be pure cellulose. The inner layers are made up of secondary cellular deposits; or are formed of a gradual thickening of the outer layer. The extreme end of the fibre is closed, that originally attached to the seed is broken off irregularly.

We have here a fibre which from its natural constitution may materially complicate the normal action of dyeing. All the natural fibres are complicated in their physical formation.

If all the fibres in a pound of cotton were placed end on, they would extend to 2200 miles.

Within the limits of dyeing temperatures, a dry heat has little, or no, influence on the fibre substance itself. The material which makes up the purified cotton fibre is cellulose. This substance has been the subject of a great deal of research. Its ultimate composition is expressed by the formula: $C_6H_{10}O_5$.

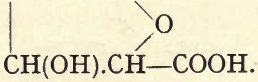
In its purest form, cellulose is regarded as an inert substance, white in colour, insoluble in all ordinary reagents, such as water, alcohol, &c.; and the action of these solvents on the fibre is said to be a negative one. At a high temperature and pressure, the fibre is, in some respects, altered by water. Zinc chloride, phosphoric acid, and ammoniacal copper solution dissolve this fibre. The precipitate from these solutions is called "regenerated" cellulose; and it has been maintained that the alteration in its substance is merely structural. This is doubtful, however, for the capacity of filaments prepared from these regenerated compounds to absorb dyes is profoundly modified. The same phenomenon is noticed with the regenerated cotton from an alkaline thiocarbonate solution. The precipitated substance is, in this case, a hydro-cellulose which also has an increased affinity for certain dye-stuffs.

Some interesting speculations have been made by A. G. Green (*Rev. Gen. des Mat. Col.* 1904, 130) on the constitution of the cellulose molecule (compare Green and A. G. Perkin, *Proc. C.S.*, 1906, p. 136).

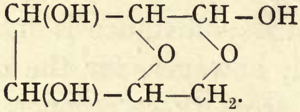
The empirical formula $C_6H_{10}O_5$ is not sufficiently complex to explain the formation of tri- and penta-nitro-compounds. This investigator considers the existence of these derivatives doubtful. The fact that cellulose can exist in the colloid state, and is difficultly soluble is not considered to indicate, as previously supposed, a high molecular weight. The same argument is not used in the case of alumina or silicic acid to explain their colloid state.

Many reasons are given to justify the simple $C_6H_{10}O_5$ formula, and the original paper must be consulted for the full details of this argument.

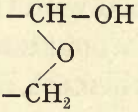
Faber and Tollens have obtained from oxycellulose dihydroxybutyric acid and isosaccharic acid:



Green proposes the following formula for cellulose:



This formula brings forward the aldehyde nature of cellulose as follows:



which by fixation of water becomes:

$$\begin{matrix}-\mathrm{CH(OH)_2}\\-\mathrm{CH_2(OH)}\end{matrix}$$

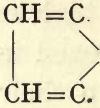
and then

$$\begin{matrix}-\mathrm{CHO}\\-\mathrm{CH_2(OH).}\end{matrix}$$

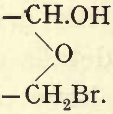
When cotton is mercerised we get an action of this order.

$$\begin{matrix}-\mathrm{ONa}\\-\mathrm{ONa}\end{matrix}\ \text{and then, finally on washing}\ \begin{matrix}-\mathrm{OH}\\-\mathrm{OH.}\end{matrix}$$

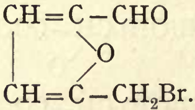
This formula is also sufficiently complex to explain the Fenton reaction, and the formation of the intermediate hydration product.



And then by addition of bromine:



And by elimination



(w. brom methyl furfural.)

From the ionic point of view, cellulose is regarded as an aggregate of ions which take their origin under special conditions present in the plant-cells in which celluloses are present as mass aggregates. The cellulose aggregate is, therefore, regarded as a mixture of ions of varying dimensions. As a consequence, cellulose as a typical colloid has no definite reacting unit as a body which takes the crystalline form, nor a fixed molecular constitution such as could be represented by a constitutional formula, the cellulose molecule not being regarded as a static unit measurable in the ordinary physical units so much as a dynamic equilibrium; its reacting unit at any moment being a function of the conditions under which it is placed.

Such is, perhaps, the most recent definition of the constitution of the celluloses from the ionic point of view as advanced by C. F. Cross.

If this view is accepted as a working hypothesis, and we regard the fibre colloids as solution aggregates rather than fixed and definite units, it may be taken for granted that the further study of the action of dyeing will throw light on this subject generally.

The two extreme views of the constitution of cellulose are expressed here, and will indicate to the student the varied nature of the ideas on this subject to-day.

Action of reagents on cotton.—Cellulose is unable to resist entirely the action of reagents.

Acids, for instance, may modify its structure and composition in a remarkable way.

The ultimate action of sulphuric acid is the production of grape sugar, but the action takes place in stages which are more or less marked. Dextrin is an intermediate compound of the same ultimate composition as cellulose itself. The first action of this acid is of a less destructive nature. The cotton fibre swells up, gelatinising at the same time. By a very rapid removal of the strong acid at this stage, so-called "vegetable parchment" is produced. This product finds important uses in the industrial world. Its strength is greatly increased and its dye affinity modified.

Nitric acid has a destructive action, if carried to an extreme stage. At a high temperature the acid breaks up the fibre and destroys it. The ultimate products are different in this case, oxalic acid being one of the final products of the reaction. The action of this acid in the cold, either in the presence of sulphuric acid or alone results in the production of nitrates. The higher nitrates being used as explosives (gun-cotton), the lower nitrates dissolve in solvents such as ether-alcohol, and are then known as collodion. They also enter into the composition of xylonite, &c. The action of dyes on these nitrated fibres is a more energetic one. A systematic examination of their relative actions on these different nitro-products is greatly needed, and has never been published. The solubility of these nitro-compounds is entirely different to that of the original cotton. As mentioned above it either swells up or dissolves in alcohol-ether. On the other hand, it no longer dissolves in zinc chloride. It is practically insoluble at low temperatures in this reagent.

The action of weak acids on cotton fibre is roughly indicated in some experiments by A. Scheurer. The fibre was subjected to a 20 grm. solution of oxalic acid; or its equivalent in other acids. The results are expressed in percentages.

DIMINUTION IN STRENGTH OF FIBRE.

Acid.	After 4 hours (cold).	After 3 days in hot air.	After steaming for 1 hour.
Oxalic . .	2.5	25.0	25.0
Tartaric . .	.0	5.0	10.0
o.-phosphoric .	1.0	1.5	15.0
m.-phosphoric .	2.5	31.5	35.0
p.-phosphoric .	2.5	35.0	35.5
Phosphorous .	1.5	27.0	28.0

The addition of such substances as glucose seems to exert a protecting influence when present in the above solutions.

For example, with oxalic acid and 50 grms. glucose to the litre, a protection equivalent to 13 per cent. occurs in hot air, and 6 per cent. on steaming, as compared with the above figures.

Mercer in his celebrated patent gives an account of the action of such acid reagents on cotton, and notices the increased effect of dyes on the same.

The action of hydrochloric acid is also a severe one. The cotton fibre falls to powder, owing to a partial, and uneven solution of the same. (Stern, *J.C.S.*, 1904, 336.) In all these cases the acid must be strong. Weak acids have little, or no effect, on this fibre, so far as their subsequent reactions are concerned.

Action of Acid Salts.—Bisulphates, or salts which are easily dissociated, such as aluminium chloride, act on cotton, if their solutions are allowed to concentrate by drying on the fibre. In such a way cotton is separated from wool and silk, and the latter recovered and used again. In the case of wool the recovered fibre is known as shoddy. A few years ago a lace effect was produced in Switzerland by weaving silk designs on a cotton foundation and subsequently " burning out " the latter in this way.

The other acid salts act in a milder way.

Action of Alkalies.—A strong solution of caustic alkali profoundly modifies the properties of the cotton fibre. Here, as in the case of sulphuric acid, a shrinking and gelatinising action takes place. A sodium compound $Na_2O.C_{12}H_{20}O_{10}$. is said to be formed. Washing in water decomposes this compound, and a hydro-cellulose remains. Within the last few years an enormous quantity of cotton has been treated in this way. If a long staple cotton be used, and the fibre "stretched," an increased gloss is obtained; in the case of artificial silk a similar result is obtained (Dreaper and Tompkins). After mercerising a greatly increased affinity for some dyes is exhibited.

The action of oxidising agents produces oxy-cellulose which also exhibits increased attraction for dyes. When treated with caustic soda solution 100 grammes of the fibre disengage heat as follows (Vignon):

Cellulose . .	.74 cals.
Oxycellulose . .	1.30 cals.

This product also gives Schiffs' reaction for aldehydes. It will, therefore, be seen that although cellulose is a comparatively inert body, from the dyer's point of view, yet it attracts dyes more readily after being subjected to the action of strong mineral acids, alkalies, or when dissolved and precipitated. Further particulars of the action of such reagents may be found in the many papers written on this subject, and in a monograph by P. Gardner, from which the following details are taken.

The mercerising action of caustic alkali solution begins at 10° B. and increases with the strength of solution up to 35° B. The temperature should not exceed 20° C. Gardner considers that to the varying chemical action is due the different results obtained with different cottons. 10 per cent. to 30 per cent. more dye is required to produce the same shade after mercerising the fibre.

It is advantageous to mercerise at a low temperature; a weaker solution of caustic soda will produce the same effect. Lefêvre (*Rev. Gen. des Mat. Col.*, 1902, p. 1) states that at the lower temperature a 35° B. solution will give a result equal to a 50° B. solution at ordinary temperatures; but with this stronger solution and refrigeration no advantage is obtained.

Kurz (*ibid.* p. 1) considers that it is advantageous to refrigerate with raw cotton, but that with bleached cotton it is not so necessary.

The heat developed on mercerising the latter is very small, but the temperature effect is more evident in the case of raw cotton, a rise of 13° C. to 21° C. being noticed in this case.

In the case of ramie and linen it is interesting to note that the action of mercerising is a different one. This is owing to the separate cells in these fibres swelling up and ultimately bursting. The surface of the fibre becomes correspondingly rough and not smooth as in the case of cotton.

Interesting results will probably be obtained by further research on this fibre and its relative dyeing properties under these conditions.

If the cellulose aggregate or molecule is an alcoholic anhydride, its chemical activity might be due to the hydroxyl groups. Various acyl and alkyl derivatives have been prepared and their relative dyeing properties determined by W. Suida (*Monatsh. f. Chem.*, 1905, 26, 413). The results show that the dyeing properties of the nucleus are not influenced by the conversion of these OH groups into the acyl or alkyl ones.

These results should be considered in conjunction with the results obtained with nitrocellulose and hydrocellulose.

Nitration of the fibre, even to the extent of the introduction of 80 per cent. of NO_2 groups, does not appreciably alter the visible structure or breaking strain of the thread. (Bronnert, *Rev. Gen. des Mat. Col.*, 1900.)

It has also been stated that the introduction of 80–90 per cent. of acetyl groups into the cellulose molecule, does not alter the original properties of the cellulose. (Cross, *J.S.C.I.*, 23, p. 297.)

Cotton is stated to act energetically as a catalysing agent (Suida, *Monatsh. f. Chem.*, 1905, 26, 413). In a mixture of benzoyl chloride and sodium hydrate the former rapidly disappears on agitating the liquid in the presence of cotton. In its absence this effect is not noticed.

The action which magnesium and aluminium chlorides exert on cotton and other vegetable fibres is stated to be due to hydrolysis, owing to the hydrochloric acid set free on rapid drying.

Only the vegetable fibres dissociate these salts. On wool magnesium chloride gives no trace of free acid, even at a temperature of 140° C. That the wool actually takes up the chloride is shown as follows.

Cotton cloth and cashmere were soaked in solutions of magnesium chloride at 13° Tw.. and aluminium chloride at 10° Tw. The samples were weighed after squeezing and the results would indicate that the chlorine, magnesium and aluminium taken up by the fibres were normal. An exception was noted in the case of the aluminium salt and wool; more acid than base being absorbed in this case. (Hanofsky, *Chem. Zeit.*, 56, 1897.)

The hydrolysing action of water is very marked at high temperatures, and under pressure.

The fibre may even be disintegrated with the formation of soluble hydration products.

When cotton is wetted by water a certain rise in temperature takes place. At first sight this might be attributed to a hydrating action, but the general results obtained on wetting inert substances (finely divided solids) does not altogether support this idea. It has long been known that a similar action takes place when these powders are immersed in inorganic or organic liquids (Pouillet). A careful study of the conditions which give rise to these phenomena has been made by Masson (*Proc. Roy. Soc.*, 74, 230). Unlike the ordinary disengagement of heat which may take place in an exothermic reaction, there is no definite limit either in time, or degree. The action sometimes persists for hours, giving an increased surface temperature of from 8° to 12° in the case of cotton. Similar temperature results were obtained in the case of glass wool in the presence of water vapour. The conclusion arrived at was that the action is a distillation effect through a layer of air ; and that this gives rise to the thermal phenomena noticed in these cases. This investigator recorded that if the solid is wetted, no temperature effect is obtained ; and concluded, therefore, that the action is not a chemical one.

The results obtained by Martini (*Phil. Mag.*, (5) 47, 329) do not, however, seem to confirm these observations. With pure silica, in a finely divided state, a great rise in temperature is recorded in such solutions as distilled water (22.6°), absolute alcohol (26°), and sulphuric ether (31.5°). Under exceptional circumstances the silica was raised from 17° to 80° C. There can be little doubt, but that the alcohol and ether actually wet the silica. Yet Masson distinctly states that glass wool will not give the temperature effect with water, but only with water vapour, on account of the air film.

Martini considered that the liquids are absorbed by the solids, and enter the solid state themselves (*ibid*. (5) 50, 618). He subsequently modified this idea, and considered the action a physico-chemical one. Silica is said to abstract water from a mixture of three parts of alcohol to one of water.

On the other hand, he notices a reverse action in the case when mercury is the liquid. The whole subject seems to be very involved in the present stage of our knowledge. Three distinct theories have been advanced to explain the action depending on distillation effect; transfer to the solid state, or a physico-chemical cause respectively.

The matter must be allowed to rest here for the present, but the ultimate solution of this problem may possibly throw light on the subject of the absorption of substances by fibres, &c., and is worthy of further attention.

The idea that a liquid can enter a solid, and by some influence be degraded to the solid state, under conditions which would normally determine the liquid one, is a far-reaching hypothesis. This effect, if really present, must greatly modify our ideas on the attractive value of fibres. Further work on this subject is urgently needed, to clear up these points.

Wool.—The standard works must be referred to for details as to the actual physical structure of the many varieties which come upon the European markets.

The fibre substance is called keratine. Its chemical constitution is obscure. The published analyses of wool vary greatly, and there is no direct evidence that keratine is a definite substance. To prove this, it is only necessary to state that the sulphur varies from 2 to 4 per cent., and that this is partly removed by dilute alkali. If strong alkali is used the wool "dissolves," and if this solution be acidified, the larger part of the sulphur passes off as sulphuretted hydrogen.

The mineral matter present, probably in combination, varies also in amount (*J.S.D. and C.*, 1888, 104) and composition. It averages a little over 1 per cent. on the weight of the wool.

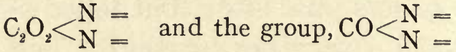
The action of dilute acids seems to be more specific than in the case of the vegetable fibres. Wool treated with sulphuric acid (or hydrochloric) and subsequently washed attracts colouring-matters with increased avidity.

Nitric acid gives with wool a yellow colouration, due to the formation of xanthoproteic acid.

Nitrous acid (Richard, *J.S.D. and C.*, 1888, 154) "diazotises" part at least of the wool fibre. Colours can be "dyed" on this by subsequent treatment with solutions of phenols and amines. The writer attempted to prepare these substances in a more or less pure state, but failed chiefly owing to the small quantities present. These "dyes" are not, as might be expected, "fast." They have little resistance to the action of soap solutions at the boil (*J.S.C.I.*, 1894–95). It is claimed that the substance in the wool fibre which acts in this way is an amido acid, termed launginic acid, by the discoverer (Champion, *Compt. Rend.*, 72, 330). To prepare this 500 grm. of carefully washed wool was dissolved in baryta solution. The filtered solution was precipitated by lead acetate. After washing the lead salt was suspended in water and SH_2 passed through the solution. The filtrate was evaporated to dryness, yielding about 6 per cent. of a dirty yellow powder. Champion gives the formula $C_{19}H_{30}N_5O_{10}$ for the acid, but Knecht and Appleyard (*J.S.D. and C.*, 1889, 71) do not agree with this, as they find that it contains 3 per cent. of sulphur. The following reactions are given: sodium acetate being present in the solution.

Alum = white precipitate.
Stannous chloride = white precipitate.
Copper sulphate = light green curdy precipitate.
Ferric chloride = light brown precipitate.

It shows the characteristic reaction with Millon's reagent. A great number of lakes have been prepared with this substance and the acid colouring-matters. Schützenberger's formula for wool based on its hydrolysis indicates that the wool molecule contains the groups



$$C_2O_2<\begin{matrix}N=\\N=\end{matrix} \quad \text{and the group,}\ CO<\begin{matrix}N=\\N=\end{matrix}$$

but does not contain any NH_2 groups. Coloured products would, however, be obtained as above by the formation of nitrosamines from the NH group. The compounds formed seem to withstand the action. The formation of these compounds will be further discussed in chap. vii. in the relation to the chemical theory of dyeing. It is considered by Knecht (*J.S.D. and C.*, 1889, 71) that the presence of this amido acid in the wool fibre in an insoluble state may be the cause of the action of dyeing. As prepared, it precipitates acid and basic dyes, tannic acid, and mordants.

Very strong mineral acids dissolve wool, and the solution gives precipitates with the acid colours.

Alkalis affect the wool fibre more or less. Very strong solutions may even dissolve it. It is stated ("Manual of Dyeing," p. 43) that alkalis are not retained so tenaciously as acids after absorption by the fibres.

The action of certain metallic salts in solution on wool is of the greatest importance from the practical point of view.

Many salts of iron, chromium, copper, and other metals seem to be decomposed in the presence of the wool substance, and the oxide or basic salt is precipitated on the wool out of the aqueous solution.

The whole subject of mordanting is a complicated one, and will be considered in chap. iv., where the probable nature of the reactions observed will be discussed.

Silk.—The silk fibre in its natural state consists of an inner and insoluble fibre or filament, making up about 70 to 76 per cent of the total weight of the fibre, and an outer coating of silk gum, or sericine. This material is soluble in caustic alkali solutions in the cold, or soap solutions at the boil. The fibroïn or silk substance is then left in its final state.

The composition of the fibroïn is, like that of all albuminoids, uncertain. Richardson (*J.S.C.I.*, 1893, 426) considers the mass formula to be

$$C_{14}H_{16}(CO.OH)_3.CO.OH(NH_2)_5$$

and considers that the graphic formula is of the following order:

$$x\begin{matrix}\diagup NH.CO \diagdown \\ \diagdown CO.NH \diagup\end{matrix}x$$

x representing a carbon residue.

There is, however, no satisfactory evidence that this residual fibre is of a simple nature.

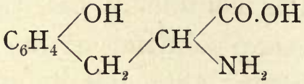
The ultimate analysis of mulberry leaves, silkworms, sericine and fibröin are as follows:

	Leaves.	Worms.	Sericine.	Fibröin.
C	43.73	48.1	42.6	48.8
H	5.91	7.0	5.9	6.23
N	3.32	9.6	16.5	19.00
O	35.44	26.3	35.0	25.00
Mineral matter .	11.6	9.0	—	—

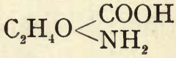
It is possible that the sericine or silk gum is a more soluble oxidation product of the fibroïn and may possibly be formed in the following way:

$$\underset{\text{Fibroïn}}{C_{15}.H_{23}W_5O_6} + H_2O + O = \underset{\text{Sericine}}{C_{15}H_{25}N_5O_8}.$$

Cramer by the action of dilute sulphuric acid on silk gum obtained 5 per cent. of tyrosine (hydroxy-phenyl-*a*-amido-propionic acid).



and 10 per cent. of amido-glyceric acid,

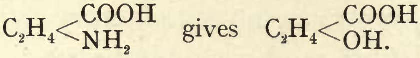


$$C_2H_4O<\begin{matrix}COOH\\NH_2\end{matrix}$$

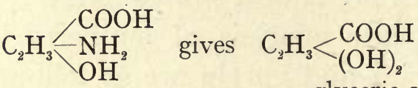
This body like silk has a neutral reaction and combines with both acids and bases.

This body which has been called sérene ($C_3H_7NO_3$) is very similar to alanine ($C_3H_7NO_2$).

By the action of nitrous acid the former gives glyceric acid, and the latter lactic acid.



$$C_2H_4<\begin{matrix}COOH\\NH_2\end{matrix} \quad \text{gives} \quad C_2H_4<\begin{matrix}COOH\\OH.\end{matrix}$$

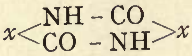


$$C_2H_3\begin{matrix}\diagup COOH\\-NH_2\\\diagdown OH\end{matrix} \quad \text{gives} \quad C_2H_3<\begin{matrix}COOH\\(OH)_2\end{matrix}$$

glyceric acid.

Therefore, sérene may be a mono-amido-glyceric acid

Representing fibroïn as



$$x<\begin{matrix}NH-CO\\CO-NH\end{matrix}>x$$

on saponification with KOH it would give:

$$2x<\begin{matrix}NH_2\\CO.OK\end{matrix}$$

Some further work has been done on this subject by Fischer and Skita (*Zeit. f. Phys. Chem.*, 1901, 177, and 1902, 221).

By decomposing boiled off silk by hydrochloric acid, the following substances were obtained (per 100 pts. of fibroïn).

10 pts.	β-tyrosine
21 ,,	δ-alanine
36 ,,	glycocoll
1 to 1.5 pts.	β-leucine
,,	β-phenylalanine

Traces of diamino acids were discovered in the products of hydrolysis, and arginine was recognised among them. Serine is also one of the decomposition products of fibroïn as well as of sericine.

Sericine yields hydrolytic products from which a considerable quantity of diamino-acids may be separated by dialysis, arginine being among them.

These authors consider that the difference between fibroïn and sericine is only a quantitative one. The same mono-amino acids are obtained from both. In addition to tyrosine and serine, they obtained leucine and phenylalanine from them.

The well-known diazo reaction has been applied to the animal fibres, and effect colours may be produced on silk, by subsequent development with phenols, amines, &c. The colours do not seem, however, to be fast to either washing or light. The colours produced on wool are duller than those from silk.

This matter is more fully entered into in chap. viii.

One part of sodium nitrite was found to be sufficient to "modify" fifteen parts of wool.

The resulting, and modified fibre is very sensitive to light, and change of temperature, like many of the diazo compounds. On boiling with water it takes a brown colour. The same shade is produced by the action of dilute sodium hydrate solution. The alkaline carbonates act in the same way, but less energetically. The treated wool is said to show an increased affinity for basic colours and a decreased one for acid ones. This property may even be made use of in printing to obtain different shades with the same dyes.

This special property is lost in sunlight. An exposure of only a quarter of an hour to diffused light will bring the wool back to its normal state so far as this action is concerned.

Nitrite of soda itself, without the usual addition of acid, will act on wool at 100°–110° C.; a characteristic orange-rose colour being produced under these conditions on the fibre.

Many aromatic oxy-derivatives will give colour effects on the fibre, in the same way as phenols, and amines, after treatment with nitrous acid.

Flick and Bourry (*Bull. de Soc. de Mulh*, 1889, 21) consider that this action is rather due to the presence of NH. than NH_2 groups in the fibre compounds.

The action of acids and alkalies on silk are therefore in a way similar to those obtained with wool.

The physical differences due to apparent solution may be noticed when strong solutions of the reagents are used. It is probable that hydrolysis takes place, and that through this, the physical structure is destroyed and the colloid enters the pseudo solution state.

Owing to their complex nature our knowledge of the composition of the fibre substances is very limited, and, from our point of view, unsatisfactory.

It is, therefore, difficult to formulate the relations of these bodies to the dyes and mordants during the time of dyeing, with any certainty, by arguing from their supposed chemical constitution. We must rather look for evidence of a more indirect nature, to determine the reactions between these animal fibres and dyestuffs generally.

CHAPTER III

DYES AND LAKES, AND THEIR PROPERTIES

THE rough division of dyes into two groups, the one containing the natural dyes, or those which are the more or less direct products of organic life; and the other the artificial dyes, enables us to dispose of the former group in a few words.

The nature of these dyes, and the state of impurity in which they exist in the numerous extracts, which serve in the ordinary dyeing operations, renders it very difficult to discuss their action.

It may be stated that these vegetable dyes are not present in the growing plant. They exist there as chromogens, which are mostly colourless. These yield their colouring-matters by subsequent oxidation, fermentation, &c.

Some of the products like indigo, madder, orchil, and logwood are, or have been, of great value in the dyeing of woollen and other goods, but they are being gradually replaced by new products.

Of recent years a good deal of work has been done on the constitution of these dyes when prepared in a state of purity. The results obtained are hardly of sufficient interest, having little bearing on the action of dyeing, to claim our attention in the present work.

We may, therefore, pass on to the so-called artificial dyes, the first of which was introduced by Dr. Perkin in 1856.

This dye, mauveine, created a great sensation at the time of its introduction. In 1859, Verquin introduced fuchsine. Since that time the list has increased by ever-varying shades and dyes of new constitution, until, to-day, we have at our disposal a range of colouring-matters, which will respond to almost all the requirements of the dyer, as regards fastness and application. It may be interesting here to review the different ways under which these dyes have been classified.

Bancroft's scheme, which in the past has received general acceptance, divides the dyes into two classes.

(1) Subjective.

(2) Adjective.

The first class includes those colours which will dye without a mordant. The second class includes those which require one. In the present day it is difficult to accept this simple classification. Some dyes may even belong to both classes.

Von Prager used the terms dye and dye-stuff respectively to describe the dye materials belonging to these two great classes.

Hummel, on the other hand, taking note of the many colours which may be produced by means of different mordants, has called the two classes of dyes monogenetic and polygenetic.

With the great increase in number, and properties of the dyes used in the present day, v. Georgievics has fallen back on the divisions which are generally accepted as representing their actions, viz.:

Acid dyes.
Basic dyes.
Dye salts.
Sulphur dyes.
Vat dyes.
Mordant dyes.
Developing dyes.
Albumin dyes.

Even this extended classification has obvious defects.

With our increasing knowledge a modification of O. N. Witt's classification, which is of a more scientific nature, and depends on the constitution of the dyes, may ultimately be accepted.

This method divides the dyes into classes depending on the presence of certain groups from which there is evidence that their specific characters are chiefly derived. These he calls the chromophorous groups. These form the so-called chromogens, which make up the root, or stock substance of the dyestuff.

These chromogens are converted into dyes by the introduction of salt-forming substances.

For instance:

$—N = N—$ is a chromophorous group.
$C_6H_5—N = N—C_6H_5$ is a chromogen.
$C_6H_5—N = N—C_6H_4.NH_2$ is a basic dye.
$C_6H_5—N = N—C_6H_4.OH$ is an acid dye.

This classification does not indicate the action of the dye in detail. In fact, it would be very difficult to do this.

From the point of view of dyeing, it is possible that some scheme of classification will be possible in the future, which will include classes depending on their physical state in solution, in conjunction with their chemical properties (*see* chap. x.). It is at least a fact that all the dyes are either acid, or basic in their nature; or contain both acid and basic groups at the same time.

The OH and NH_2 groups which give to the dyes the acid or basic properties, are naturally of the greatest importance. In the above scheme, these groups are called auxochromes. They also seem to play a part which leads to the production of coloured compounds.

Another group, which is so often present in the dye molecule, is the sulphonic acid radical (HSO_3). The introduction of this group into the molecule is generally brought about with the object of rendering the dye more soluble in water, and not with the object of producing colour. As a matter of fact, the reverse action is generally noticed. The sulphonic acids of many dye-stuffs are deficient in tinctorial power when compared with the non-sulphonated products.

This is by far the commonest way of bringing the azo dyes within the range of practical solubility. There are, however, other methods of arriving at the same result. Geigy states that the introduction of a trialkylammonium group has this effect.

All azo compounds are coloured, but all of them are not dyes. Their chief value is in the fact that they are chromophores and can be converted into dyes by Griess' reaction, which consists in diazotising the amine and combining the product with phenols, amines, &c.

This reaction is not, however, capable of universal application. The constitution of the azo compound may determine otherwise. The amidopyridines are an example; only the beta derivative can be readily diazotised.

Also, if the amido groups are in the ortho position as regards the azo group, the compound is incapable of diazotisation.

As a general rule a phenol, or amine, will enter the para position as compared with another OH, or NH_2 group. If, however, the para position is already occupied it will take up the ortho position.

If both the ortho and para positions are filled it will probably form no dye-stuff.

By double entrance of the diazo group the production of tetrazo dyes is effected.

Generally speaking the simpler dyes are yellow or greenish in yellow, but as the molecule increases the colour changes to orange, then red, violet, or blue. A simple example of this which is known to all dyers is seen in the azo dyes produced from primuline on the fibres. It will be remembered that the following results are obtained:

With phenol, a golden yellow shade.
With resorcinol, an orange one.
With β-naphthol, a red one.

Nietzki was the first to notice the general nature of this action and Schultze to confirm it.

The actual cause of the production of colour is not understood.

Armstrong favours the idea that the quinone structure is directly connected with the production of colour in this class of compounds. The evidence, however, does not seem to be complete on this point.

Discussing the question of constitution and colour, Green (*J.S.C.I.*, 1893, 12, 3) has pointed out that the leuco- or reduction-compounds of various dyes exhibit a striking difference of behaviour on exposure to air.

Disregarding those colours which are entirely split up by reduction, viz., the azo, nitro, and nitroso colours, it is possible by this action to classify colours into two groups.

(1) Colours whose leuco-compounds are not readily oxidised on exposure to air.

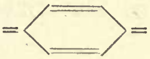
(2) Colours whose leuco-compounds are rapidly oxidised on exposure to air.

Group (1) consists of the triphenylmethane series, the phthaleins or pyrone colours, the indophenols and the indamines.

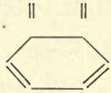
Group (2) contains the indigo class, azines, azonium colours, oxazines, thiazines, acridine colours, the thiazol, quinoline and oxyanthraquinone colours.

Accepting Armstrong's theory that colour is due to the quinonoid structure of the molecule.

The colouring-matters of the first group may be regarded as paraquinonoid,



and those of the second group as ortho-quinonoid.

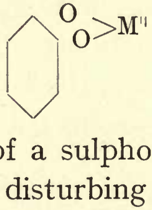


This view is confirmed (*Proc. Chem. Soc.*, 1890, 222; Armstrong, *Proc. Chem. Soc.*, 1888, 4, 27; 1892, 8, 101, 143, 189, 194).

The cause of some colours being mordant colours seems to have been determined beyond dispute.

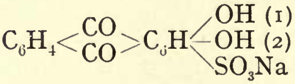
The presence of OH or CO.OH groups is essential to the production of these colours. The position of these groups is also a matter of importance. It is necessary that the two hydroxyl groups shall be in the ortho position. One carboxyl group may take the place of one hydroxyl group.

The normal group may, therefore, be taken as



The introduction of a sulphonic acid group into the dye molecule has a disturbing effect on the formation of metallic lakes.

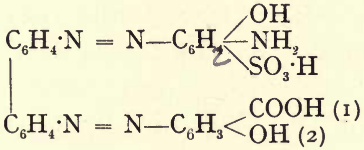
For instance, Alizarine red S (powder) is



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H\begin{matrix}/OH\ (1)\\-OH\ (2)\\\backslash SO_3Na\end{matrix}$$

The addition of copper sulphate to a solution of this dye will not produce a lake or precipitate. If, however, the corresponding barium salt is produced by adding barium chloride to the solution before the addition of copper salt a precipitate is obtained (Dreaper, *J.S.C.I.*, 12, 272).

In the same way, Diamine Fast Red F. will also give a lake with copper sulphate if the $\cdot SO_3$ group is in combination with barium. The action of the sulphonic acid group is effective in preventing the lake formation, even although it is far removed from the lake-forming group, as will be seen in this particular case.



$$\begin{array}{l} C_6H_4\cdot N = N\text{—}C_6H_2\left\langle\begin{matrix} OH \\ NH_2 \\ SO_3\cdot H\end{matrix}\right. \\ | \\ C_6H_4\cdot N = N\text{—}C_6H_3\left\langle\begin{matrix} COOH\ (1) \\ OH\ (2)\end{matrix}\right. \end{array}$$

It is difficult to explain the cause of this action. It may be found, perhaps, in the greater solubility of the sulphonic acid, and the partial neutralisation of this effect by formation of a barium salt.

The presence of an amido group may also materially interfere with the formation of lakes, even if the OH groups are present in the ortho position. It would almost seem that here the action is of a different nature, the acid nature of the $\left[\begin{matrix}\text{—}OH \\ \text{—}OH\end{matrix}\right.$ groups being in part neutralised by the proximity of the NH_2 group.

The reason why certain colours are mordant dyes is becoming increasingly involved.

The Liebermann and v. Kostanecki law is no longer accepted, owing to our increased knowledge on the subject since the year 1885.

Buntrock in 1901 was the first to throw doubt on this law. He discovered that derivatives of groups in the ortho position would dye on mordants. (*Rev. Gen. des Mat. Col.* 1901, 99.)

In the same year, Noelting established the fact that bodies like hystazarine and quinizarine (dihydroxyanthraquinones, 2. 3 and 1. 4), also 1. 3. 5. 7 tetrahydroxyanthraquinone, and 1. 8-hydrodioxy-2. 4. 5. 7, tetranitrochrysazine were also capable of being mordant colours.

V. Georgievics in 1902 pointed out that the hydroxyanthraquinones do not follow the above law.

In the years 1887 and 1889, v. Kostanecki extended and enlarged the original law which then stood as follows :

(1) Nitroso-phenols are mordant colours when in the ortho position.

(2) Phenolic colours dye on mordants when they contain two OH groups in the ortho position.

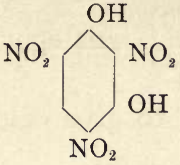
(3) Orthoquinonedioximes are mordant colours.

(4) Ortho-oximes are mordant colours.

In the year 1904, Moehlau and Steimmig (*Rev. Gen. des Mat. Col.* 1904, p. 360) return to this subject. The following law is propounded. In an aromatic hydroxyl derivative when an OH group is in a position near to the chromophore, the body is a mordant dye.

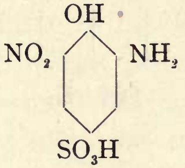
Picric acid is not a mordant because the compounds with metallic oxides are soluble.

But trinitro-resorcinol



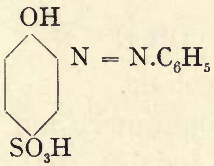
dyes wool on chromium or iron mordants, shades which are very fast against the action of soap.

Nitro-amido-phenol-sulphonic acid

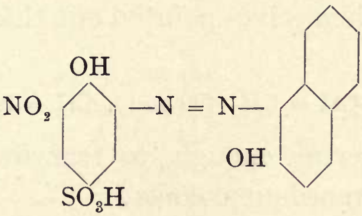


dyes wool, on chromium, iron, or aluminium mordants and the shades also resist the action of soap.

Ortho-hydroxyazo-benzene-*p*-sulphonic acid.



and nitro-phenol-sulpho-azo-β-naphthol

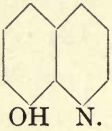


both dye on these same mordants.

Quinonoid Colours.—From the point of view of colour the group $\begin{matrix}\text{NOH (1)}\\ \text{NOH (2)}\end{matrix}$, is equivalent to $\begin{matrix}\text{OH (1).}\\ \text{NOH (2)}\end{matrix}$

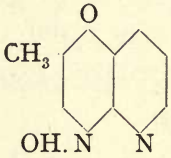
The group $\begin{matrix}\mathrm{OH} & (2)\\ \mathrm{O} & (1)\end{matrix}$, analogous in grouping to $\begin{matrix}\mathrm{OH} & (2)\\ \mathrm{NOH} & (1)\end{matrix}$, seems also to give colouring-matters the property of dyeing on mordants.

Noelting and Trautmann have found that 8-hydroxyquinoline and its derivatives



are mordant colours.

6-Methyl-5-keto-8-isonitrosoquinoline



is also a mordant colour.

In a further communication Prud'homme (*Rev. Gen. des Mat. Col.*, 1904, p. 365) doubts whether this rule of Moehlau and Steimmig can always be applied; they having themselves pointed out that the chromophores

$$-\mathrm{CH}=\mathrm{CH}-\mathrm{CO} \text{ and } -\mathrm{CH}=\mathrm{N}-$$

are not powerful enough to transform ortho hydroxyls into mordant colours.

He also points out that Scheurer had previously shown that dehydrated mordants will not combine with mordant dyes.

Quite recently, further investigation tends to show that in some cases alizarine lakes are not chemical compounds. (W. Biltz, *Ber.* 1905, p. 4143.)

From a study of their formation, alizarine iron lakes are said to be of the nature of chemical compounds; but Alizarine Red S.W. lake on chromium oxide is said to be formed by absorption.

It may be that these lakes resemble the tannic acid ones, or are similar to Linder and Picton's dye compounds (*Trans. Chem. Soc.* 1905, p. 1934), where both actions seem to be involved.

The formation of alizarine lakes may be due to solid solution, absorption, or they may be chemical compounds.

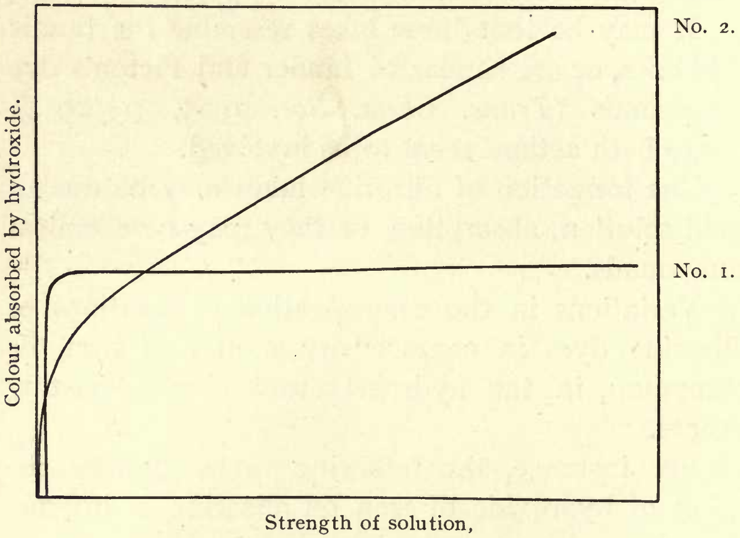
Variations in the concentration of solutions of alizarine dyes in contact with oxides of iron, or chromium, in the hydrogel state, give interesting results.

For instance, the following table, showing the effect of hydroxide of iron on alizarine, is instructive.

Initial concent. of bath.	End do.	Col. abs. per grm. of hydroxide.
.0005	.00114	.0677
.01	.00234	.134
.02	.00242	.308
.04	.00261	.655
.06	.0028	1.01
.10	.00326	1.695
.15	.00369	2.57

In the case of Alizarine Red S.W. on chromium hydroxide, the following results were obtained:

Initial concentration.	End do.
.01	.00034
.02	.0031
.03	.00776
.05	.01876
.075	.0341
.10	.05
.50	.417

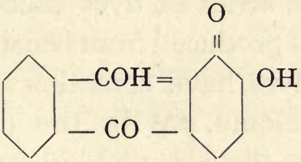


FORMATION OF LAKES IN AQUEOUS SOLUTION.

The relative nature of the reactions indicating chemical action, or absorption, respectively, is seen in the above curves. No. 1 indicates chemical action in the case of an alizarine iron lake, and No. 2 absorption in the case of alizarine on chromium hydroxide. The decreased absorption of alizarine dyes on a dehydrated mordant, as compared with the same mordant in a highly gelatinised state, is shown in the following ratios :

Alizarine	1/6
Gallein	1/11
Alizarine Yellow G.G.W. .	1/9.5

It is suggested that the reason why alizarine will not dye in the absence of lime is that it is necessary for the alizarine to be in the quinonoid state, and that this state only occurs in the presence of alkali.



It must always be remembered, that the alizarin aluminium lake may not be so insoluble as the double calcium one.

To decide in practice whether a dye belongs to the mordant class it should be sufficient to make experiments with wool mordanted with the following metals: aluminium, iron, chromium, copper, and tin. The value of the mordant dye will, of course, depend on the brilliancy and fastness of the shades produced. These are most important factors, especially from the wool-dyer's point of view.

In the case of the nitroso dye compounds the ortho position between the O and —NOH groups is essential to a mordant dye.

In some cases dyes which possess an OH group in the ortho position with regard to azo groups, may possess the property of dyeing on mordants.

This action, in which closer grouping evidently gives rise to what may be termed a more concentrated effect, is an instructive one. It gives us an insight into the structure of the molecule. Closer grouping seems to be more favourable to combined action. This is seen in the two nitro-salicylic acids, and the relative acid nature of the 1. 2. 3 and 1. 2. 5 compounds (*J. C. S.*, 88, 338) respectively.

The typical dye, Congo Red, which led to the discovery of the series of dyes which dye vegetable fibres directly, is produced from benzidine; and hence this series of dyes have sometimes been known as the benzidine colours. With the extension of this class, and from their varied origin, they are now known generally as "cotton dyes," or sometimes as "direct dyes."

Generally they are prepared by diazotising certain bases; and combining the products with amines, phenols, or their sulphonic acids.

Sometimes the dyes are mixed products. In the preparation of these, advantage is taken of the fact that the first molecule of the amine, &c., is taken up at a greater rate than the second one. In this way these mixed products are easily prepared.

V. Georgievics, in discussing the possible cause of the attraction of the cotton fibre for these dyes, has pointed out that it cannot be due to the presence of the diphenyl group, for certain dyes only possessing one azo group are known to dye cotton without a mordant.

The so-called sulphur dyes have recently become of great importance in cotton-dyeing, on account of their fastness and the ease with which they can be applied.

The sulphur dyes originated with the researches of Croissant and Bretonniere about thirty years ago. Sawdust, horn, &c., were fused with alkali and sulphur. As a result, products soluble in water were obtained which were capable of dyeing yellow brown shades. This substance was known in commerce as Cachou de Laval.

To-day, the class of sulphur dyes is an extensive one, and they are classified by Pollak as follows :

(1) Dyes from simple benzene and naphthalene derivatives.

(2) Dyes from diphenylamine derivatives.

(3) Dyes from anthraquinone derivatives.

(4) Dyes made by the help of sodium thiosulphate.

(5) Dyes made by the help of chloride of sulphur.

This classification is a rough and ready one, but the chemistry of the subject is very involved. The fact that it is almost impossible to isolate the intermediate compounds, which are formed during the manufacture of the dyes, renders it very difficult to follow the change which take place. Vidal, Meyenberg, Green, and Perkin have attempted to throw light on this most interesting subject. Vidal believes that sulphide dyes produced from compounds of simple structure, and at low temperatures, are probably thiazine derivatives.

These sulphur dyes are insoluble. They are brought into solution by dissolving in sodium sulphide. At the same time, they are reduced to their leuco-compounds, so that subsequent oxidation is necessary to reproduce the colours *in situ.* This may be brought about in some cases by simple exposure to the air; or in others by the use of oxidising materials, such as hydrogen peroxide.

Instead of sodium sulphide, neutral sodium sulphite has been recommended as a solvent, and is used in conjunction with glucose and alkali, which serve to reduce the dye to the leuco condition. The addition of salt to the dye-bath greatly increases the dye fixed. The other insoluble dyes which are produced in the fibres, such as indigo, or aniline black, present interesting problems to the student.

From the fact that they are produced by oxidation, the dyeing process is probably of a physical nature.

The production of aniline black on the fibre is a complicated process from the chemical point of view.

Here again, the intermediate products are not easily isolated, and this makes it difficult to follow the reaction.

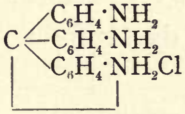
The basic dyes are usually hydrochlorides of organic bases. The combination between the base and acid is a weak one; entirely different in its nature from that of the sulphonic acid azo dyes, are very stable compounds.

These bases form lakes with tannic acid, which were at one time of great service in the dyeing of cotton goods, and are still used for this purpose;

and also in the production of lakes for pigment colours.

Although at the point of saturation, these compounds seem to combine in the ratio of their chemical equivalents in the ordinary sense of the word.

Pararosaniline hydrochloride—



—is a typical example of this class of dye.

It has also been more recently suggested that in some cases the alizarine lakes are absorption compounds (*see* page 43).

Identification of dyes.—Of the many schemes suggested, only that recently advanced by Prof. Green in conjunction with Messrs. Yeoman and Jones (*J.S.D. and C.* 1905, p. 236) is noticed here.

This scheme, like the earlier one proposed in 1893 by the first of these investigators, entails the reduction of the dyes to their leuco-compounds.

Originally zinc dust was used as the reducing agent, reoxidation being effected by exposure to air, or else by chromic acid.

Nitro, nitroso, and azo compounds were completely destroyed on reduction. Dyestuffs having an ortho-quinonoid structure gave leuco-compounds which were readily reoxidised by air to their original state. Para-quinonoid compounds giving leuco-compounds required chromic acid for reoxidation.

Sodium hydrosulphite is now recommended as a reducing agent in place of zinc dust ; and the statement is made, that the leuco-compounds formed remain in great part attached to the fibre, while washing will remove the fission products of the azo dyestuffs.

A persulphate is used in place of the chromic acid. The following general behaviour of the various chemical groups of dyestuffs is noted.

Decolourised by hydrosulphite.			Not altered by hydrosulphite.	Not decolourised but changed to brown, original colour restored by air or persulphate.
Colour restored on exposure to air.	Use of persulphate required to restore.	Colour not restored by air or persulphate.		
Azines Oxazines Thiazines Indigo	Triphenyl methane group.	Nitro-, Nitroso-, and azo-groups.	Pyrone, acridine, quinoline, and thiazole groups. Some members of anthracene group.	Most dyestuffs of the anthracene group.

Further tests with other reagents are given in the original communication with a complete range of colours dyed on wool and silk.

The point of interest is the way the leuco-compounds are held by the fibres. Further details should be of value. The action may be due to the colloidal nature of these compounds.

The different rate of solubility of dyes in different solutions is important, but before we consider this point the relative solubilities of dyes in aqueous solution at varying temperatures is given. The results are stated in grammes per 100 cc. of solution for some of the best known dyes. (Pawlewsky, *Chem. Zeit.* 73, 773.)

Dye.	20° C.	60° C.	100° C.
Martius Yellow	.002	.01	.13
Violet R.	.03	.86	27.24
Cyanine	.04	.21	1.21
Magenta	.22	1.28	12.23
Picric Acid	1.14	2.94	9.14
Erythrosine	4.56	12.7	24.58

The increase in solubility at high temperatures is great in some cases.

The relative action of picric acid in solvents has been studied with the following results. (Sisley, *Rev. Gen. des Mat. Col.* 1902, 90.)

Water	1.00
H_2SO_4 (.5% sol.)	.43
Ether	3.56
Toluene	8.60
Amyl-alcohol	1.49

The colour of the solution varies greatly. In toluene it is almost colourless, and possesses a dichroism not found in an aqueous solution.

This is attributed by Marckwald (*Ber.* 1900, 1128) to electrical dissociation. At any rate a difference in molecular state is indicated.

The following table shows the ratio of picric acid taken up by toluene and water in mixtures of the same at a temperature of 20° C.

SOLUTION MIXTURE.	RATIO TAKEN UP.
Solution 10 *grms. per litre.*	
100 cc. OH_2 .25 cc. Tol.	1 : 4.02
100 cc. ,, .100 cc. ,,	1 : 2.63
50 cc. ,, .100 cc. ,,	1 : 4.40
Solution 3 *grms. to litre.*	
100 cc. OH_2 .25 cc. Tol.	1 : 1.6
100 cc. ,, .100 cc. ,,	1 : 1.24
50 cc. ,, .100 cc. ,,	1 : 2.38
Solution 1 *grm. to litre.*	
100 cc. OH_2 .25 cc. Tol.	1 : 1.15
100 cc. ,, .100 cc. ,,	1 : 1.63
50 cc. ,, .100 cc. ,,	1 : 0.72
Solution .1 *grm. per litre.*	
100 cc. OH_2 .25 cc. Tol.	All in water
100 cc. ,, .100 cc. ,,	,,
50 cc. ,, .100 cc. ,,	,,

Sisley explains these abnormal results with dilute solutions by assuming the dissociation of picric acid in dilute solutions; this being complete at .1 grm. solution strength; and that the toluene cannot extract the colour ion.

Similar results were obtained with ether and amyl alcohol as follows:

Ratio of OH_2 to Ether or Amyl Alcohol 100 : 100.

10 grms. to litre sol.	1 : 1.79	1 : .209
1 grm.	1 : 0.129	1 : .071
.1 grm.	1 : .01	1 : .0101
.01 grm.	All in water	All in water

In these two cases we have dilution also interfering with extraction from aqueous solution. It might be pointed out that these results may be also explained by accepting the association theory of solution.

CHAPTER IV

ACTION AND NATURE OF MORDANTS

Our knowledge of the action of fibres on certain metallic salts in aqueous solutions is incomplete. The subject is one of great interest to the dyer. Many of the difficulties he has to contend with are due to variations in the mordanting processes.

Aluminium mordants.—There is a general impression that these mordants act by producing a basic salt on wool and silk fibres ; a corresponding amount of acid remaining in solution.

This may, or may not, be the case according to the varying condition of solution. Washing in water after the mordanting process is said to render the salt fixed more basic by the removal of acid, or an acid salt. The rate of mordanting may, therefore, increase with the basicity of the solution. This is noticed in practice. Many neutral and stable salts are said to be free from any action of this nature, and will not act as mordants.

The influence of the basicity of aluminium salts on the actual absorption results is indicated in the following table. Aluminium sulphates were prepared, and solutions containing 200 grms. per litre of the respective salts were taken. The fibre was cotton. (Liechti and Suida, *J.S.C.I.* 1883, 537.)

Composition of sulphate used.		% Al_2O_3 taken up.
$Al_2(SO_4)_3 + 18H_2O$ (normal)	..	12.9
$Al \cdot (SO_4) \cdot (OH)_6$	..	51.0
$Al_4 \cdot (SO_4)_3 \cdot (OH)_4$	..	58.7
$Al_2 \cdot SO_4 \cdot (OH)_4$	..	—

The last and most basic salt dissociated so rapidly, that the experiment could not be completed.

It will be seen that a slight increase in basicity over the last salt mentioned would produce an insoluble compound on the cotton fibre irrespective of any combination with the cotton fibre itself. Some of these salts have been prepared, and are insoluble. These experiments are not so complete as they might be. The composition of the salts precipitated on the fibre has not been ascertained. They have only been expressed in terms of the hydrate.

The fact that these basic salts cannot be obtained directly by the addition of alumina to the normal sulphate is important. There does not seem to be any tendency for the solution to redissolve any alumina actually precipitated in the fibre.

The fact that a salt is a basic one is not, however, any indication that it will act as a mordant. Basic chlorides and oxychlorides of alumina can be prepared, yet they are very indifferent mordants. Very little of the metal can be fixed on the cotton fibre by solutions of these salts.

On the other hand, the sulphites and thiosulphates of alumina are available as mordants.

The basic thiocyanates, and the acetates and sulphacetates are of great value.

In practice, it is advisable to supplement the direct fixing action of the fibre, by some secondary reaction. For instance, suitable substances may be present, which in themselves form insoluble compounds by loose combination with the alumina. As an alternative process the mordanted fibre may be passed through a suitable alkaline bath. Such materials as oil mordants, or tannic acid, are used as a preliminary treatment. Their action is sufficiently clear. The alumina is sometimes fixed as arsenate, phosphate, or silicate. It is worthy of note that all these precipitates are of a colloidal nature.

Turkey red mordanting.—The process of fixing alumina on the cotton fibre assumes fresh importance from the fact, that the mordant must contain fatty acids in some shape, or form.

The modern method of dyeing Turkey red, differs materially from the older processes of dyeing which originated in the East, many years ago.

Le Pileur d'Alpigny published an account of these older processes in 1765.

The original process took between three and five weeks to complete, and it is quite unnecessary to try and follow the many operations entailed. To-day Turkey red may be dyed in three days, or even less, using artificial alizarine in the place of madder, and soluble oils in the place of olive oil, or other fatty matters of a more or less obscure nature.

Alizarine (dihydroxyanthraquinone), $C_{14}H_8O_4$, may be regarded as a weak dibasic acid. It is even capable of decomposing sodium acetate. It contains two OH groups in the ortho position.

It combines with most of the metallic oxides forming insoluble lakes. A serious study of these compounds has been undertaken by Liechti and Suida (*J.S.D. and C.* 1885, 271; 1886, 102, 120, 131, 146) and the chief results obtained are as follows:

Alizarine combines with calcium to form normal or basic alizarates as the case may be. At a high temperature, or if a solution of the basic alizarates be heated, the normal salt, $C_{14}H_6O_4 \cdot Ca$, is always formed.

On the other hand, the aluminium lakes are formed with great difficulty in the absence of calcium salts. The presence of ammonia helps the reaction. Basic aluminium alizarates are formed, and are more insoluble than the normal salt.

In the production of a Turkey red on cotton, it is essential that a compound lake of aluminium be formed. A great many of these have been prepared, varying in their properties and reactions. The normal lake is $(C_{14}H_6O_4)_3\ Al_2 \cdot (CaO) \cdot H_2O$, and is readily soluble in ammonia.

In practice the alizarine lake is a compound of alizarine, calcium, aluminium, and fatty acids and therefore little can be said of the actual composition of these lakes as present on the fibre.

The actual operations entailed in the production of this colour are said to be as follows ("Manual of Dyeing," p. 558):

(1) Oiling.
(2) Sumacing.
(3) Mordanting.
(4) Dyeing.
(5) Clearing.

(1) To-day, little seems to be used for oiling but the so-called sulphated oils. These are probably sulphonic acids. At any rate, their usefulness lies first in their solubility in water, and, secondly, in the fact that they are readily decomposed by steam, &c. Bodies similar to the oxidation products produced from olive and castor oils in the older processes are said to be formed at the same time. This has, however, been denied.

(2) The object of sumacing is to introduce tannic acid into the fibre in order that it may subsequently precipitate and hold a larger proportion of alumina.

(3) The mordanting operations consist of treating the fibre with aluminium salts; and subsequently completing the fixation of the alumina on the fibre.

(4) The dyeing which follows these operations supplies the alizarine, and lime necessary. A minimum temperature of 70° C. is necessary to complete the formation of the lake.

(5) The clearing operations are generally two soapings. These remove any impurities, and here the formation of the lake is also modified.

At this stage stannous chloride is sometimes added to give " fire " to the colour. It is generally supposed that this does not enter the lake, but simply acts physically. Tin oleate is formed which acts as a varnish on the fibre. A certain proportion of the fatty acids in the soaping solution is fixed on the fibre.

This roughly represents the action and process of dyeing Turkey red.

Further light has been thrown on these reactions by Persoz (*Bull. Soc. Ind. de Mulh.* 1903, 193). When mordanted cotton is dyed with 2 grms. of 10 per cent. alizarine, and an equivalent quantity of lime per litre, a deep red colour is produced in a few minutes. If at this stage the fibre be washed and dried, the shade produced is a dull yellowish brown. If this be treated with a fatty acid and steamed, a bright red colour is produced.

If, on the other hand, the dyeing is prolonged to say one hour, this brightening action will not take place. These experiments indicate that there are two possible modifications of the compound lake of alizarine, alumina, and lime. The former can be transformed into the latter by steaming, and will not then develop; nor can it be reconverted into its first form by any known means. It is, of course, just as easy to argue that when the final and saturated lake is formed it will not combine with the fatty acids. The first " modification " may simply be a compound still containing aluminium in a state capable of combining with the fatty acids. This explains the object of having the fatty acid present before the mordanted fibre enters the dye bath. It is well known that the so-called alizarine reds, which are dyed with subsequent oiling, are inferior to Turkey reds in fastness, and colour effect.

The chief constituent of the modern soluble oils is said to be ricinoleic acid, free or combined with alkalies. Boiling the oil with dilute hydrochloric acid decomposes the sulphonic acid compound liberating this acid. (Noelting and Binder, *Bull. Soc. Ind. de Mulh.* 1888, 730.)

On the other hand, the superiority of soluble oil prepared from castor oil over that from olive oil is stated to be due to the fact that in the former case an acid sulphonic ether of an unsaturated acid is present. In the latter case we have the corresponding derivative of a saturated acid. This is held to indicate that the former product will have a higher oxidising power and consequently be a better mordant for this purpose. (Benedikt and Ulyer, *Monat. Chem.* 8, 208.) Further research must decide which of these views is the correct one.

Prepared in the pure state the above ricinoleic acid gives lakes, as bright as those prepared with the oleins.

Purified aluminium ricinoleate after drying is pulverulent. Its formula is $Al_2O(OH)_2(C_{18}H_{33}O_3)_2$.

This compound heated with water and alizarine begins to attract the colouring-matter at 40° C., It then melts and gradually assumes a bright red colour, while the temperature is being carried up to 105° C.

This would seem to indicate that it is necessary for the fatty acid to melt before it can enter into combination. This lake is unaltered by boiling soap solution. Alcohol and ether dissolve this lake with difficulty, and then cotton may be "dyed" with this solution. It would be interesting to know something of the fastness of the colour, dyed in this very mechanical way. Fischli (*ibid.*) also denies that oxidation takes place in the fixing of ricinoleic acid on the fibre. This he confirms by analysis. He also shows that mere heating in dry air will not "develop" the colour of the lake, but if steam is present, the colour develops instantly. Microscopical examination shows that steam favours the formation of the alizarine-lime-alumina-fatty-acid lake. Immediately after the steaming, the cloth has a sticky feel partly due to the melting of this lake. In this way it penetrates the fibre. It is also contended that tin, if present in the soap liquor, actually enters into combination with the mordant.

One of the most extraordinary statements made in connection with the formation of these lakes is that light is an important factor in the formation of the fatty mordants. (Storck and Coninck, *Bull. Soc. Ind. de Rouen*, 1887, 44.) Much work remains to be done on this subject.

Iron mordants.—The lakes formed with alizarines are quite fast, and not dependent on either the presence of lime or fatty acids for their colour, although the latter greatly aids in the fixing of the iron, and lime is distinctly beneficial.

It is stated that the iron must be introduced into the cotton fibre in the ferrous state and oxidised *in situ*. If not, the colour is not fast. It is known that many dyes are much faster if produced *in situ*, but this is the only known case where a mordant acts in the same way.* A ferric ferrous compound may be produced in the case of alizarine, and is said to have the following constitution $(C_{14}H_6O_4)_3Fe_2 \cdot FeO$.

The fact that mordants are for the most part of a basic nature was noticed as early as the year 1849 by Gonfreville. When cream of tartar was used he considered that it entered into the composition of the lake, and in some way, or other, prevented the "rubbing off." Acids were considered to lessen the affinity of the wool for the mordant, and at the same time to increase the power of diffusion.

Rouard and Thénard (*Ann. de Chimie*, 74, 267) held the idea that wool could not decompose alum, but simply absorbed it. It could all be removed by boiling water. The fibre would decompose cream of tartar on boiling, acid being taken up and neutral tartrate left in the solution. He considered that wool boiled with tartar and alum might contain alum, tartrates of alumina, potash, and free tartaric acid.

Later on, Chevreul denied that the alum could be washed out by water, and Bolby stated that actual decomposition took place; a basic salt being deposited on the fibre leaving the solution more acid. Schützenberger considered that wool exerted some special attractive force retaining the alum in this

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* If the mineral colours are excepted.

way. The idea that the wool precipitates the basic alum by removing the acid from the solution was first put forward by Liechti and Hummel. (*J.S.C.I.* 13, 357.) The addition of organic acids, or acid salts, was said to prevent the too rapid precipitation of the resulting basic salt on the fibre.

They considered also that the appearance of a well mordanted wool points to the presence of a salt, and not a hydrate.

These authors also support the idea that a salt is precipitated, by pointing out that in "single bath" dyeing the liquid is always acid. It is difficult, however, to see the connection between these two operations. In the latter case the already formed lake is present, the acid playing the part of a more or less active solvent, as in the case of a logwood-iron lake; or else by directly influencing the fibre state.

Harvey pointed out in 1872 (*Monit. Scient.* 1872, 598) that in the case of very concentrated solutions of alum, more sulphuric acid than alumina is absorbed. This has been recently confirmed by v. Georgievics. It appears that with a 24 per cent. solution of alum, and a proportion of water to fibre of 30 : 1, alumina and sulphuric acid are taken up in their normal proportions. The affinity of wool for acid is stronger in dilute solutions, and stronger for the alumina in strong solutions. The relative curves cross each other at 24 per cent.

Although wool will take up large quantities of sulphuric acid from concentrated solutions of this acid, yet in dilute solutions water plays the part of a base just as it precipitates basic salts from solutions of the heavy metals.

Alum is said to be so far dissociated in solution that the whole of the SO_3 can be titrated with sodium hydroxide using phenol-phthalein as indicator (Carey Lea). It is also noticed that wool mordanted with alum reacts acid; the indication is that the acid is present in the free state.

Chromium salts.—The mordanting of wool by bichromate was at one time simply regarded as a case of absorption, the bichromate being taken up by the fibre. The idea that the bichromate splits up into a chromate which remains in solution, and chromic acid which is absorbed by the fibre is put forward by E. Knecht. (*J.S.D. and C.* 1889, 186.) It is assumed that the chromic acid combines with one of the fibre constituents to form an insoluble chromate. This has been disputed, it being held that the dissociation of the salt is due to the presence of ammonia, due to the decomposition of the fibre material on boiling.

Knecht found that the ammonia given off is not sufficient to account for more than a thousandth part of the change. He also denies that the presence of alkaline salts in the wool bring about the action. Taking a sample of wool and mordanting it after treatment with hydrochloric acid, he found the chromium distributed as follows:

Total bichromate in solution . .	.030	grm.
Total chromate	.112	,,
Chromic acid on wool . . .	.057	,,

He does not uphold Nietzki's assertion that a chromate of chromium is formed in the fibre. It is held that if this action, which is represented by the following equation, took place serious damage to the fibre must result.

$$5K_2Cr_2O_7 + 5H_2O = 2Cr_2(CrO_4)_3 + 10KOH + 3O_2$$

He agrees that a certain amount of oxidation goes on, but that it is not of this order.

Whatever the state of the chromium, it is capable of easy reduction. This is practised by immersing the mordanted wool in sulphurous acid.

The action of assistants in chromium mordanting such as tartaric, oxalic, or sulphuric acids is said to be primarily that of the liberation of chromic acid .Tartar, lactic acid, and oxalic acid also act as reducers.

It is necessary that the mordants shall be properly fixed on the fibres, and shall not be merely precipitated on the surface.

The presence of sulphates, chlorides and other salts in the mordanting bath prevents the dissociation of the mordant salt.

The state in which dichromate of potash is present in aqueous solutions has been studied by Abegg and Cox (*Nature*, vol. 71, 281). They determined the proportion of free chromic acid present in solutions of different strengths, the presence of chromic acid being indicated by the following reaction:

$$K_2Cr_2O_7 \rightleftarrows K_2CrO_4 + CrO_3.$$

Complete dissociation is calculated to take place at a dilution of 1000 litres. At greater concentrations the following results were obtained

At 100 litres . .	99%
At 10 litres . .	91%
At 1 litre . .	62%

These figures indicate, that the greater part of the salt is decomposed into chromic acid, in solutions corresponding in strength to those used in mordanting wool.

In the mordanting of cotton, for alizarine, it has been shown that the presence of calcium salts as well as aluminium salts is necessary.

It is also found necessary to have a metallic monoxide present in the case of wool-dyeing (Möhlau and Steimmig). With pure alumina mordant on wool, no lake formation seems to take place in the absence of calcium, barium, strontium, or magnesium compounds. The same effect is noticed with iron mordants. In this case magnesium gives the best results. It is said that the same effect may be noticed with chromed wool.

Chromium chloride, and chromium fluoride, are both used for mordanting wool. Little is known about the nature of the reactions in these cases.

Iron mordants on cotton and wool have received little attention from the theoretical point of view. The probable nature of the reactions may be taken to be of a simpler nature than in chromium mordanting.

Copper mordants.—The results obtained by these mordants in practice is satisfactory, but little is known of the actions which take place. Copper finds little use except in the case of wool-dyeing. No figures are available which indicate in any way the course of the reaction in this case. It may simply be a case of absorption. On the other hand, basic compounds may be fixed in the fibre; or some chemical action may even take place, which leads to the same result.

Other metallic mordants.—Little is known as to the actions involved in the use of these compounds.

Some of them give satisfactory shades, and leave little to be desired on the score of fastness, but beyond this our knowledge does not extend.

The salts of nickel and titanium are of interest in this connection.

Tannic Acid.—This substance is of the greatest value to the dyer of cotton and some other vegetable fibres.

The well-known property of tannic acid of forming lakes with basic dyes is taken advantage of. The vegetable fibres also seem to have an attractive power for this acid, perhaps because of its colloid properties. The fact that antimony tannate gives faster lakes with the basic dyes, is perhaps against any theory of direct chemical combination between the acid and the fibre.

O. N. Witt holds (*Chem. Zeit.*, 12, 1885) that in these lakes there is no distinct molecular ratio between the colour base, and the tannic acid. There seems to be a definite saturation point, however, for a solution of night blue has been used volumetrically for the estimation of tannic acid by direct precipitation.

These lakes are soluble in excess of tannic acid, and also in acetic acid. The latter reaction is sometimes made use of in printing, the acetic acid being subsequently driven off by heat.

The lakes containing antimony are more resistant to the action of alkali.

The tannic acids are little used on wool, and on silk they play the part of a dye, rather than a mordant. The bleached acid has a use in the weighting of light colours on this fibre, and in blacks the amount of tannin lake held by the silk fibre is of an extraordinary nature in some cases.

The action of tannic and gallic acid on fibres generally is entered into more fully elsewhere.

A series of results obtained by observing the action of different mordants on silk both in the "raw" and "boiled off" state are given by P. Heermann (*Farb. Zeit.* 3, 1903). The mordants chosen were basic ferric sulphate, basic chromium chloride, acetate of alumina, and stannic chloride. The influence of time on the mordanting process is indicated in the table on p. 68. The figures given indicate the increase of weight of 100 parts of fibre.

It is unfortunate that these experiments were not conducted on such lines that the composition of the precipitated mordants could be given.

The decrease in the weight of mordant fixed during the period of seven, and fourteen days, may

IRON, CHROMIUM AND TIN MORDANTS

Time.	Iron 52° Tw.		Chromium 32° Tw.		Stannic chloride solution 52° Tw.	
	Raw Silk.	Boiled off Silk.	Raw Silk.	Boiled off Silk.	Raw Silk.	Boiled off Silk.
1 min.	7.07	1.84	3.55	1.91	6.44	11.69
15 min.	8.00	4.01	6.38	3.03	10.36	17.73
30 min.	8.76	4.18	7.16	3.75	11.98	17.80
1 hr.	9.05	4.32	8 56*	3.72*		
2 hrs.	9.20	4.92	—	—	14.53	17.91
6 hrs.	9.69	5.10	11.00	4.32	16.58	18.71
24 hrs.	9.95	4.89	12.47	6.13	18.45	19.85
48 hrs.	9.79	4.98	14.35	7.24	16.28	19.06
96 hrs.	9.75	5.03	14.39	—	16.03	19.16
7 days	9.79	5.03	14.47	7.57	14.78	18.20
14 days	9.87	—	—	—	14.88	17.34

* 1½ hours.

be due not so much to a decrease in the percentage of metal deposited, as to the same being in a more basic state.

The influence of temperature on the mordanting process is indicated in the following table (*Farb. Zeit.* 8 and 9, 1903):

COMPARATIVE AMOUNTS TAKEN UP AT DIFFERENT TEMPERATURES.

	Per cent. increase of maximum increase.							Actual increase.
	0° C.	5°	10°	15°	20°	25°	30°	per cent.
Tin								
Raw Silk .	74.5	83.5	86.5	89.4	93.3	97.5	100	18.93
Boiled off .	100	100	100	100	100	100	100	16.0
Iron								
Raw Silk .	62.6	68.1	77.8	84.3	90.3	95.3	100	7.85
Boiled off .	100	100	100	100	100	100	100	4.95
Chrome								
Raw Silk .	100	100	100	100	100	100	100	11.38
Boiled off .	69.1	72.9	78.4	86.8	92.6	97.2	100	5.83
Al.								
Raw Silk .	39.1	54.5	66.4	84.7	100	100	100	1.43
Boiled off .	81.4	85.6	92.0	95.5	100	100	100	3.12

(Tin and iron solutions 52° Tw. Cr. 32° Tw. Al. 15° Tw.)

The effect of the condition of the mordanting bath as regards its basicity is important. Heermann defines the "basicity number" of a mordant as the ratio of absolute acid content to the absolute metal content; *e.g.*, the number for stannic chloride is

$$4 \times 36.45 \div 118.5 = 1.23.$$

The influence of additions of acid and alkali to the normal mordants, stannic chloride, chromium chloride (basic), $Cr_2Cl_3(OH)_3$, basic ferric sulphate, and aluminium acetate is as follows: the addition of alkali in all cases resulted in considerably more mordant being absorbed, but the addition of acid did not always produce the opposite effect. With tin and aluminium a very slight decrease was noted; iron, on the other hand, showed a rapid decline, 5 per cent. of acid decreasing the absorption value to one-half. In the case of chromium also a rapid drop was noticed. That is to say, the influence of acid on normal salts is small, but its influence on basic salts great.

In concluding this work, Heermann examined the five theories which have been put forward to explain the mordanting process, in the light of the following facts (*Farb. Zeit.* 1904, 15, 165):

(1) Nature of fibre has a great influence on the result.

(2) Mordants cannot be rubbed, or boiled off.

(3) Duration of treatment, temperature, and state of solutions, have great influence on ultimate result.

(4) Efficiency of mordant not proportional to its ionisation.

(5) Temperature of bath increases during mordanting action.

(6) Chemically indifferent compounds take part in the process.

(7) Fibre not altered structurally, or chemically by the process.

(8) The basicity of mordant remains constant during the process.

(9) Mordant base on the fibre is capable of further combination and reaction.

(10) Ratio between weight of mordant and fibre, influences the result of operations.

Of the theories put forward to explain the action of mordanting Heermann prefers the ionic one to the impregnation, solution, "organo-metallic" or the catalytic ones which are considered less satisfactory. Light may be thrown on this subject by the further study of the reactions of substances in the colloidal state.

CHAPTER V

STATE OF FIBRES AND ACTION OF ASSISTANTS

The condition of the fibres at the time of dyeing is a most important factor in the production of satisfactory results, especially where even dyeing and fast colours are required.

It matters little whether the action of dyeing is of a physical or chemical nature. In either case the fibre must be presented to the dye solution in such a condition, that an even and equal absorption of the dye-stuff will result. All parts of the skein, or piece of woven material, must be equally acted upon by the assistants present in the dye-bath, when these tend to influence the fibre state.

The problem of equal dyeing seems to entail three essential factors: (1) The state or condition of the fibre; (2) The conditions of dyeing; (3) The condition of the dye solution. It is therefore essential that the fibre substance shall be free from all impurities, natural, or acquired during the preliminary processes of manufacture.

Fibres are subjected to the action of many substances, or solutions, with the object of attaining this end.

It is advisable to consider the action of these different reagents on the impurities known to be present in the natural fibres; and to allow for any possible action of these reagents themselves, on the purified fibre substances met with in commerce.

In any specific case, those reagents which remove the impurities, and leave the fibre in a homogeneous state, of good colour and lustre, will be most suitable for that special material, and lead to satisfactory dyeing results.

It is hardly necessary to state that these conditions are never entirely satisfied in practice. The processes in vogue at the present time which make up this preliminary treatment, are briefly considered under the headings of the respective fibres.

Silk.—This fibre comes into the markets in what is called the "gum" or raw state.

The silk fibre or "boiled off" silk is obtained in a pure state by treating the raw silk with a hot solution of some alkali or soap.

In practice this is brought about by boiling the silk in one or more soap solutions, with subsequent thorough washing with soft water.

The soap solution should be carefully made up with a neutral soap. A soap made from olive oil is generally considered to be a satisfactory one. If any free alkali be present it must be in small quantities, or the gloss of the fibre will suffer.

In these hot baths, the silk gum is rapidly removed, and leaves the fibroïn in a suitable condition for the subsequent operations of mordanting and dyeing.

The original harshness of the raw silk disappears, and the surface of the fibroïn is shown in all its beauty.

In the dyeing operations which follow, it is important that the fibre shall be free from insoluble soaps.

Great care is therefore taken to remove all soap from the fibre, and to protect the silk against any surfaces which might introduce dirt, or oil.

Owing to the absorptive power of silk, iron is easily taken up by the fibre, and this action must be particularly guarded against in the choice of dye-vessels, &c.

Although many substitutes for soap have been suggested for "boiling out" the silk, yet in this country, at least, it is almost universally used.

Such materials as borax, sodium carbonate, sodium sulphide, and other weak alkalies, are possible substitutes for soap in the boiling-off process, but they do not leave the silk in such a satisfactory state, the strength and brightness of the fibre not being so good.

The following figures indicate the relative boiling-out action of sodium carbonate in distilled water and soap solution (5 per cent. sol.).

The time of boiling-out was a quarter of an hour, and the temperature 95° C.

Sample I.	Per cent. of sodium carbonate.	Per cent. of Gum removed.	
		In water.	In soap sol.
1	.02	7.2	—
2	.05	13.0	—
3	.07	19.1	—
4	.11	19.3	—
5	.15	19.6	—
6	.0	—	22.1
7	.01	—	22.2
8	.04	—	22.9
9	.07	—	23.2
10	.15	—	23.4

The use that the "boiled off" liquor is put to in the subsequent process of dyeing is also an important factor in favour of the use of soap. In the presence of the silk gum the soap solution may be acidified without any separation of fatty acids. This emulsion has a "levelling up" action, and tends to prevent uneven dyeing when it is added to the dye liquor. The only other preliminary treatment which "boiled off" silk may be subjected to is a bleaching process. Where the yellow raw silk is used this is necessary for light colours.

The operations entailed are not of a complicated nature, but the action of the bleaching reagents on the composition of the silk itself has not been determined.

Hydrogen peroxide and sulphurous acid are the more commonly used agents. Permanganates are occasionally used, as also is nitrous acid.

The silk fibre is therefore usually presented to the dye bath in a hydrated, and slightly alkaline state. It is free from grease or wax. The efficiency of soap for boiling out is probably due to the presence of free alkali in small quantity in the liquor. Lime, or magnesium salts, in the water may lead to the formation of insoluble soaps, and uneven dyeing.

The silk itself may contain these substances. A preliminary acid bath will remove them.

We know that alkalies are held by silk against the action of water in common with many other substances.

This makes it difficult to obtain the boiled-out silk fibre, in a uniform condition, for purposes of investigation and until further work has been done it is impossible to suggest a standard method of boiling out silk for this purpose.

It is clear that experiments in the past have been performed on the fibre, which has been treated in different ways.

It is suggested that silk skeins for special work should be first treated at 95° C. with a 1 per cent. solution of olive oil soap, followed by a further treatment with $\frac{1}{2}$ per cent. solution for half an hour, with subsequent washings in very weak ammonia (1 c.c. to 1000 c.c.), and three or four washings in distilled water at 40° C. This will give a fairly pure sample of boiled-off silk. The temperature of the boiling-off solution should not be above that indicated.

The action of excess of free alkali, if present in any quantity, on silk or wool, is decidedly harmful. The silk itself is attacked with loss of strength and lustre.

The action of alkali on wool at high temperatures is of a similar nature.

The effect of boiling wool for one hour in a solution of alum, acidified with sulphuric acid, causes considerable hydrolysis (Gelmo and Suida, *Monatsh. f. Chem.* 26, 855). There is considerable loss in weight and formation of soluble amino-acids. Some of the decomposition products resemble peptones in their action. These are said to interfere with the fastness of the colours, in the absence of mineral acids.

This breaking down of the fibre substance is accelerated in the presence of mineral acids. This is noticed also in alkaline solutions, as might be expected, with products of animal origin.

The action of caustic soda on wool is specific (Washburn, *J. S. D. and C.*, 1901, 261). At ordinary temperatures wool is increased in strength in the ratio of 55 to 41 when soaked in an 82° Tw. solution. At the same time 84 per cent. of the sulphur present is removed. The lustre and feel are said to be improved, and the affinity for dyestuffs increased. Treatment with alcoholic potash, with subsequent slight acidification and washing is said also to give a similar result, on dyeing with direct and azo dyes. (Gelmo and Suida, *ibid.*)

It will therefore be realised that these preliminary processes may materially modify the subsequent operations of dyeing, &c., by direct action on the fibre substances themselves.

The processes used in preparing vegetable fibres, by reason of their more inert nature, may be correspondingly drastic.

Of the preliminary operations in the treatment of wool fibre the objects to be attained seem to be fairly simple. In the unwashed state wool consists of the fibre proper, which is protected by wool fat and the suint, or yoke.

Thoroughly cleaned wool seems to have the same composition as horn, or feathers. This substance has been named keratin. It is a proteid.

The wool fat is peculiar in its way. It contains no glycerides. It is chiefly made up of cholesterin, isocholesterin, oleic, stearic, and other fatty acids.

The suint contains about 40 per cent. of inorganic matter. It chiefly consists of potash salts of stearic and oleic acids, besides phosphates, silicates, &c., in smaller quantities. The object of the preliminary operations is clearly to remove these from the fibre.

The fatty and wax-like bodies may be removed by light spirits, such as petroleum ether. The potash salts may, of course, be removed by water.

Soap and soda are chiefly used to wash wool. The temperature should not be above 40° C.

The operation of bleaching wool may modify its composition, or may merely change the colouring-matter. The figures given elsewhere indicate that the latter is quite possible.

Sulphurous acid and peroxide of hydrogen are the two substances used for bleaching wool.

The former may be used in the form of the gas (stoving), or else in aqueous solution.

The basis of hemp, flax, jute, ramie, &c., is cellulose more or less lignified. Oils, resins, and colouring-matters have to be removed. Cellulose, although a carbohydrate, like starch, is very resistant to the action of ordinary solvents, which may, therefore, be used in the preparation of these fibres.

Dilute acids, and alkalies, are used for this purpose. In the absence of air the action of the latter solutions is reduced to a minimum.

In the preliminary preparation of these fibres they are submitted to a retting process. A series of changes brought about chiefly by bacterial action takes place. As a result the fibre is freed from certain binding substances.

The purified flax is pure cellulose. Bleaching is difficult with this fibre, and dyes are not so readily taken up as by cotton.

Ramie (china grass) in a purified state is cellulose, and is easily bleached to a beautiful white shade.

The general action of bleaching vegetable fibres is an obscure one, and demands further attention.

Sodium hypochlorite is superior in many ways to the calcium compound. No tendering of the fibre is noticed with it. This is probably due to the presence of a smaller quantity of free hypochlorous acid.

The attraction of cellulose for water is of a definite nature. It is a property of the cellulose substance itself, and is independent of structure. Dissolved and reprecipitated cellulose exhibits the same phenomenon. (Cross and Bevan.)

The hydrating action seems to be a function of the OH groups in the cellulose molecule. As they are suppressed by combination, so this property is said to decrease.

A study of the conditions of hydration indicate that the process is a continuous, and reversible one. Cellulose in the state of hydration is more readily attacked by reagents, and absorbs larger quantities of certain dyes.

Cross and Bevan have stated that cellulose which has been artificially dehydrated by alcohol shows a greater resistance to reagents.

This hydrating action may be carried so far that actual solution seems to take place. The cellulose is said to be present in a gelatinised form. (Erdmann, *J. Pr. Chem.* 76, 385.) Cramer has, however, shown that this conclusion does not agree with the osmotic pressure of the solution. This is not, however, a fatal objection to this view.

The action of alkalies on cellulose at high temperatures has been examined by H. Tauss (*J.S.C.I.*, 1889, 913; 1890, 883). Cross and Bevan group the celluloses in their action as follows:

(*a*) Those of maximum resistance to hydrolytic action, and containing no directly active groups.

(*b*) Those of lesser resistance, and containing active CO groups.

(*c*) Those of low resistance, *i.e.*, more or less soluble in alkalies, &c.

To the first class belongs the typical cellulose, such as flax, hemp, ramie, &c. The second class contains the oxycelluloses, and the last class the non-fibrous celluloses.

The lignocelluloses (jute) are unsaturated compounds. They form definite compounds with chlorine. The action of jute in dyeing is noticed elsewhere.

The many operations which cotton has to go through in these processes are partly due to original defects, and partly due to those acquired in the manufacture (oil, grease, &c.). They include: boiling in water, boiling in lime-water under pressure, treatment with dilute acid, boiling with resin soap, bleaching, treatment with weak acid, thorough washing, and drying.

The lime is said to form compounds with the fatty acids; to remove certain substances; and to act on the natural impurities, so that they are more easily removed by subsequent operations.

The object of the next acid bath will be obvious. The effect of the following bath, soda lye, is to remove fatty acids.

Boiling with this reagent is said to be the essential process to render cotton wool absorbent (Kilmer, *J.S.C.I.*, 1904, 967).

The loss of weight on boiling cotton with caustic soda solution is indicated in the following table.

Strength of solution.	Loss on boiling for	
	Half-hour.	One hour.
1 per cent.	4.41 per cent.	5.71 per cent.
2.5 ,,	5.08 ,,	7.33 ,,

Resin soap is added to the lye-bath when the cotton is to be printed.

The action of bleaching with bleaching powder, and subsequent acid bath, are processes which bring about changes in the colour of the impurities, and to a certain extent an oxidation of the cellulose itself.

The importance of equal bleaching is evident from this point of view. The theory of bleaching has been considered by A. Scheurer in more or less detail.

The additional attractive power of hydrated cellulose (hydrocellulose) for dyes, must also be considered. This action has been noticed by many observers, including Schaposchnikoff and Minajeff (*Zeit. f. Farb. und Text. Ch.*, 1903, 13; 1904, 163), and Hübner and Pope (*J.S.C.I.*, 1904, 404). The iodides seem to be capable of replacing caustic soda in mercerising. If the fibre be soaked in a strong solution of potassium iodide, and subsequently washed with alcohol, 15 per cent. of the salt is retained. After removing this with water the fibre shows increased affinity for Benzopurpurine 4 B; but no increased effect for basic dyes.

Twelve hours treatment with boiling water will also greatly increase the dyeing effect of cotton for 4B and decrease it for methylene blue (*ibid.*).

It will therefore be seen that the fibres are very sensitive to changes in either composition, or nature, when they are subjected to the action of solutions. Even in the case of water itself this action is very evident. Mere handling will at once show that the physical conditions have greatly altered. The dyer is most concerned with the action of aqueous solutions, but the action of other solutions is of great interest from a general point of view.

When considering the action of different solutions on animal fibres during the process of dyeing, especially at high temperatures, it is instructive to note their effect on solutions of albuminoid bodies.

Some albumins may be salted out of their solutions by sodium chloride, or sulphate. Others are not acted on by these reagents.

Ammonium sulphate will, however, precipitate or salt out nearly all the proteins.

Hollmann considers that the point of concentration at which a salt begins to precipitate an albumin, is just as characteristic for these substances, as is the point of saturation in a crystalloid.

Prolonged boiling with dilute acids, or alkalies decomposes the albumins, forming among other substances a series of amino acids, including tyrosine and leucine, and diamino acids such as ornithine and arginine.

So far as their reactions with salts of the heavy metals go, they act like acids, and form precipitates.

Some albumins are said to yield insoluble compounds with weak acids, and may therefore be said to behave like a base.

They absorb tannic, picric, and phosphotungstic acids in this way.

The acidic and basic properties of these albumins, are said to recall those of the pseudo acids and bases.

These reactions are of interest to the dyer. Fibres of animal origin undoubtedly assume the hydrogel condition on boiling with water.

From a study of the general reactions we may obtain an insight into the possible results of treating these fibres in a similar way, and of varying the conditions of the liquors at the time of dyeing.

Very little real work has been done on the subject of the action of assistants in dyeing operations. This subject embraces what may be termed the action of such reagents as acids, alkalies, neutral and acid salts, &c., on the absorption of the dyes by the fibres, and on the fibres themselves.

The nature of these actions is in many cases obscure, and it can hardly be said that in any case it is fully understood.

From the practical point of view, this study is of the greatest importance. It is only necessary to instance the action of the addition of acid to the bath in the case of dyeing silk, or wool, with acid colours; or the addition of salt to the bath in the direct dyeing of cotton with the direct cotton dyes to obtain darker shades.

The first attempt to determine the relation between acids and fibres was undertaken by Mills and Takamine (*J.C.S.*, 1883, 144).

Their research on this subject was divided into two parts. The rate and amount of absorption of individual acids by silk, wool, and cotton, was first determined; and then the relative absorption of the acids by the fibres, when more than one acid was present.

In the case where more than one acid was used, the results obtained were of special interest.

For instance the following table shows the results obtained with mixtures of sulphuric and hydrochloric acids with wool and silk fibres, the ratio of absorption being shown.

Proportion of H_2SO_4 to HCl.	Wool.		Silk.	
	H_2SO_4.	HCl.	H_2SO_4.	HCl.
1 to 1	5.0	32.5	6.63	.87
1 to 2	11.3	25.5	5.0	2.5
1 to 4	16.56	18.4	4.0	3.5

These figures at once show that the addition of the second acid influences the absorption figure of the first one.

The writer of this book has made an extended series of trials with acids of varying nature. If mixtures of hydrochloric acid and, say, tartaric acid are used, the estimation of the relative absorption of the two acids is an easy one. The former acid can be estimated in two ways, viz., by $^n/_{10}$ sodium carbonate solution, and by $^n/_{10}$ silver nitrate.

After allowing for a certain amount of hydrochloric acid, which blank experiments indicate is present in the combined state in the solution, the writer could not trace any selective action of the fibre for the stronger acid, as might be expected if the general action was equivalent to any chemical action of an ordinary nature, such as might be anticipated if the amino acids in the fibres entered into the reaction. These figures are not completed at the present time.

Mills and Takamine found that the rate of absorption of the acids when present in the ratio of H_2SO_4 : 4HCl by wool and silk is expressed by the following figures :

RATE OF ABSORPTION

Fibre.	H_2SO_4.	HCl.
Wool . . .	100	179.6
Silk . . .	100	175.0

The maximum absorption ratio for silk and cotton, on the other hand, is given as follows :

Acid.	Cotton.	Silk.
H_2SO_4 . .	1	2.6
HCl . .	1	2.2
NaHO· . .	1	2.2

In the case of wool and silk the former takes up much more acid, but they both absorb about the same quantity of sodium hydrate.

When wool is treated with weak reagents separately in the proportion of HCl : NaHO, the absorption is in the ratio of 2HCl : 3NaHO.

In the case of silk and cotton the absorptions are in each case 3HCl : 10NaHO.

It is argued from this that there is some intimate relation between cotton and silk. It would be more accurate, however, to assume that the action as represented by absorption of acids is a similar one in both cases.

It would be of value to find out whether the relative absorption of acid and basic dyes, follows these figures. They should clearly do so if the actions are identical ones.

The figures for wool, silk and cotton, therefore, stand as follows:

Wool . .	HCl.	1.5 NaHO
Silk . . .	HCl.	3.3 NaHO
Cotton . .	HCl.	3.3 NaHO

The writer found when repeating some of these results that in the case of silk the absorption of acid reaches the maximum very rapidly. It is complete in a few minutes. After this no further alteration in the ratio between acid in solution to acid in fibre, took place.

So far as the experiments went, temperature had little effect on the action, but these matters are under investigation.

If the action of acid, and alkali, is a specific one, depending on the presence of amido acids in the fibre, it must follow the laws of ordinary chemical action. It is perfectly legitimate to argue from this action to that of dyes, when comparing their action on fibres.

The methods of estimating the absorption are definite, and, so far as can be seen, beyond question. The following results obtained with sulphuric acid solutions and wool are of interest.

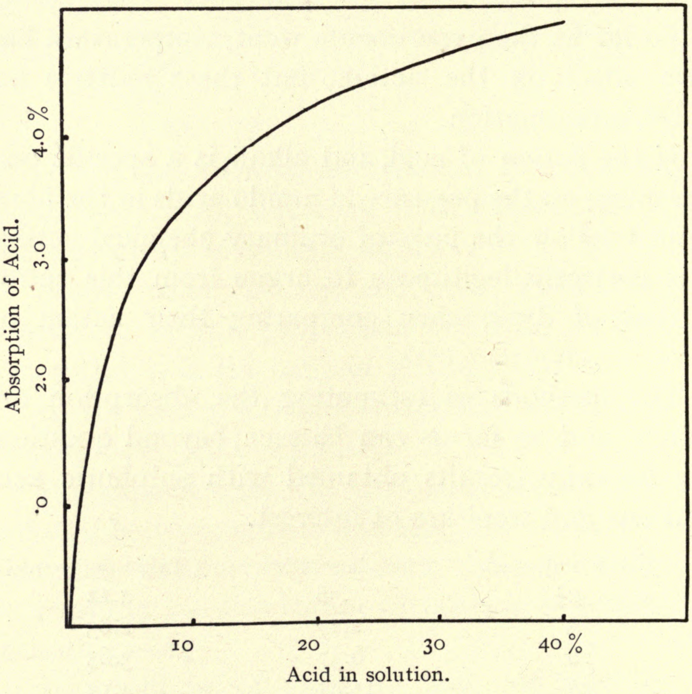
% Acid employed.	% Left in solution.	% Taken up by wool.
2½	.38	2.12
5	2.17	2.83
10	6.37	3.63
20	15.87	4.13
40	35.18	4.82

These figures should be extended ; several results should be shown between 0 and 2.5 per cent. acid and the amount extended to, say, 200 per cent. There is a certain amount of evidence that there may be two causes of absorption, but nothing is definite.

Up to 40 per cent. the maximum effect is not reached.

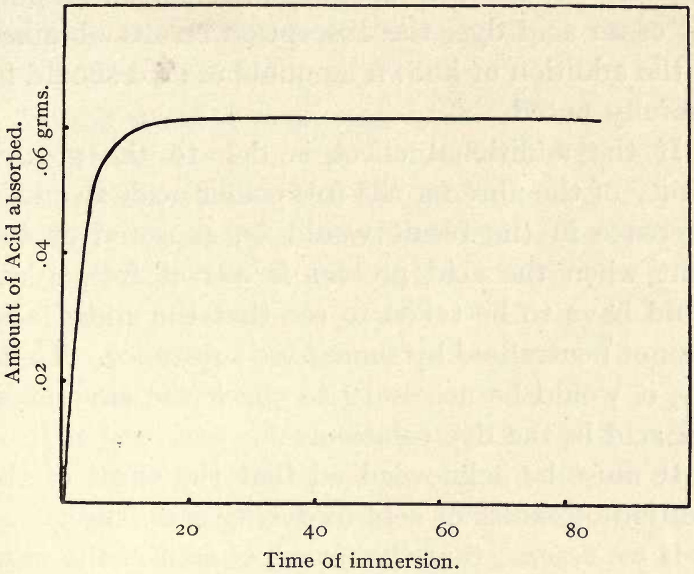
Repeated extraction does not remove all the acid, but there are no reliable figures on this subject.

The general effect will be better seen in the following curve which is plotted from the above numbers.



ABSORPTION OF SULPHURIC ACID BY WOOL.

The influence of time on the absorption of sulphuric acid in the cold (4°C.) is shown in the following curve. (Mills and Takamine.)



INFLUENCE OF TIME ON ABSORPTION OF ACID.

[OH_2. 250 cc.: Wool 2.61 grms.: H_2SO_4.6625 grms. Time unit ¼ hour.]

Action of Acids in Dyeing. Acid colours.—The generally accepted theory here is that the sodium salts of the sulphonic acids are decomposed, and the dye acids set free. This action certainly takes place, and is an important one, but from the chemical point of view has not been satisfactorily settled. From a practical point of view the excess of acid over and above the amount required to set all the dye acid free, seems to be of even greater importance. All silk dyers know that an excess of acid in the dye-bath has a pronounced effect on the rate of absorption, and the amount of dye absorbed.

A great deal of work has yet to be done on this subject. For instance, starting with silk, and a pure salt of an acid dye, the absorption results obtained by the addition of known amounts of acid should be carefully noted.

If the additional effect is due to the greater affinity of the fibre for the free colour acid, a sudden difference in the result would be expected at the point when the acid present is all set free. Care would have to be taken to see that the added acid was not neutralised by some fibre substance. To do this, it would be necessary to check the amount of free acid in the dye solution.

It must be acknowledged that the effect of the addition of excess of acid in dyeing is obscure.

If we assume that the excess of acid in the solution is taken up by the fibre substance chemically, we should expect a decreased affinity for the dye acid. The effect of the addition of a second acid in the experiments of Mills and Takamine shows that this is the result produced in practice. Increasing the ratio of the one acid to the other *decreases* the amount of the second acid absorbed.

The result obtained with the colour acids in the presence of excess of a mineral acid is of the opposite nature. The amount of the dye absorbed is increased. It is possible that the acid modifies the state of the fibre either chemically or otherwise, and that this must be taken into account, as well as possible changes in the solution state of the dye.

Quite recently some work has been done on this subject by Gelmo and Suida (*Monatsh. f. Chem.* 26, 855), which seems directly to contradict some of the previously recorded results.

Using *purified* wool, and dyeing with free colour acids of Crystal Ponceau, Lithol Red, Fast Red R., and Alizarine Yellow G.G.W., the intensity of the resulting shade is said to be independent of the presence, or absence, of free mineral acid in the dye bath.

The authors consider that the *rôle* played by the excess of acid is that of neutralising the lime, combined with the acid groups of the wool.

The writer has observed that with silk this action can be directly seen, by allowing this fibre to remain in contact with deci-normal hydrochloric acid solution, and subsequently titrating with both $^n/_{10}$ alkali and $^n/_{10}$ silver nitrate solutions. The results indicate that all the hydrochloric acid remaining in the solution is not in the free state. This complicates the estimation of the absorption of acids by fibres, and must be allowed for.

It has been noticed that wool treated with sulphuric acid and subsequently washed has a considerably decreased affinity for basic dyes, but its affinity for acid dyes is increased.

If the wool is washed with hot water, and trials are made with alcoholic solution of sulphuric acid it is found that the subsequent absorption of basic dyes is slightly more in the case of hot water washing than when cold water was used. In the case of aqueous sulphuric acid the reverse action is noticed.

On the other hand, the affinity for acid colours is considerably increased after washing with hot water, in the treatment with sulphuric acid, in either aqueous, or alcoholic solution.

Very similar results are obtained with hydrochloric acid. On the other hand, treatment with acetic acid under these conditions has little effect. The wool after washing behaves like the untreated samples.

On boiling wool with a sulphuric acid solution of alum, considerable hydrolysis takes place, with loss in weight, and the formation of soluble amino acids is said to be the final result of the reaction.

Wool treated with alcoholic zinc chloride (.1 per cent. sol.) and washed shows a decided loss in affinity for basic dyestuffs, and a greater affinity for Azofuchsine G. (acid colours). This effect is more pronounced than when an aqueous solution is used.

The effect of a preliminary treatment with either alcoholic, or aqueous, sulphuric acid before mordanting is said to be as follows. With chromium sulphate no appreciable difference is recorded, but with aluminum sulphate stronger dyeings are obtained. On the other hand, weaker shades are produced with sulphate of iron on subsequent dyeing.

Wool mordanted in this way also shows a reduced affinity for basic dye-stuffs, and an increased affinity for acid ones.

Treatment with ammonium carbonate solution is said to reverse the action of the mordanted fibre.

This secondary effect of acids is clearly seen in some experiments on the absorption of β naphthol sulphonic acid R. The amount absorbed by wool is greatly increased by the presence of sulphuric acid. (Hirsch, *Chem. Zeit.* 13, 432.)

The action here, if a chemical one, must be on the wool, and here again we might look for the opposite result to that which actually takes place. A careful study of this phenomenon is greatly needed.

The action of acids in dyeing with basic colours is even more complicated than in the case of acid dyes.

Sulphuric acid is said to impede the dyeing of wool with strongly basic dyes (magenta, methylene blue, &c.), but to promote the action of slightly basic dyes like Light Green SF, and Acid Magenta. Hydrochloric acid acts in the same way (Gillet, *Rev. Gen. des Mat. Col.*, 1900, 4, 327). The fixing action of acids seems to be inversely proportional to the basicity of the dye-stuff.

The action here from a chemical point of view is very obscure. There seem to be two possible explanations of this action.

(1) That a more stable salt is produced with the more strongly basic dyes, and that consequently the amount of base absorbed will be less.

(2) That the formation of basic salts, which are insoluble, in the fibre, is prevented; or even that if the base itself is precipitated, or fixed, in the fibre it is redissolved in the presence of excess of a strong acid.

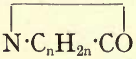
A weaker acid like sulphurous acid is said to have no action on the dyeing of wool.

On the other hand Prud'homme (*Rev. Gen. des Mat. Col.*, 1898, 2, p. 209) gives the following table which indicates that the opposite is the effect produced in practice. The table shows the altered attraction of wool for dyes after treatment with sulphur dioxide and hydrogen peroxide. Typical acid and basic dyes were taken, and the maximum dyeing effect taken as = 100.

Experiments.	Treatment.	Intensity of colour.	
		Basic colours.	Acid colours.
1	SO_2	50	40
2	SO_2 and H_2O_2 . . .	100	50
3	SO_2 and Na_2CO_3 . .	30	100
4	SO_2 and H_2O_2 and Na_2CO_3 .	80	90
5	Water only . . .	20	70

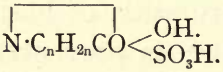
These figures indicate a possible cause for the results of uneven bleaching or dyeing in practice.

Assuming that the wool molecule has in its constitution the group



$$N\cdot C_nH_{2n}\cdot CO$$

it is claimed that the above results are explained. The treatment would probably lead to the formation of



$$N\cdot C_nH_{2n}CO<\begin{matrix}OH.\\SO_3H.\end{matrix}$$

Our knowledge of the action of acids is in a very elementary state. The results recorded are very contradictory, and indefinite in their nature. This is specially the case with the sulphonic acids, be they dyes, or otherwise. Green, on the one hand, states that with the exception of dehydrothiotoluidine sulphonic acid he could not find any colourless sulphonic acids of phenols, or amines, which had any attraction for fibres. On the other hand, the results recorded by Hirsch and Vignon would indicate that they may be absorbed.

It is probable that the study of the action of assistants will do more than anything else to throw light on the general nature of dyeing.

Action of alkalies.—Beyond a general indication as to the action of these bodies on dyeing, we have little knowledge.

In silk dyeing, for instance, it might be thought that they remove the dye from the fibre by forming an alkaline, and soluble salt. The fact that they will almost equally well remove basic dyes is against this theory; and indicates that the general action is not a chemical one. They may act by increasing the solubility of the dye in the solution, or by counteracting the attraction of the fibre colloid.

The action seems to be a specific one; soap, borax, the soluble alkaline carbonates, ammonia, act in the same way, although they vary in degree. For instance, the relative action of soap and sodium carbonate on ingrain colours and direct dyes on silk is given elsewhere; also the relative amounts of a series of primuline dyes taken up by silk in soap solution under standard conditions where it seems almost impossible for the sodium salt to be decomposed. The action of these substances is an important one, but its study has been neglected. The use of these compounds in the bath itself is chiefly restricted to the dyeing of cotton with the direct dyes, and the dyeing of alkaline blue on wool or silk.

The latter example is an interesting one from the theoretical point of view, and one which seems to have been overlooked. In order to prevent the too rapid dyeing of this colour, and also to obtain even results, the dye is applied in an alkaline solution. It is, therefore, fairly certain that it is absorbed as an alkaline salt, and consequently without combination with the fibre substance. A weak acid will subsequently set the colour acid free.

Action of neutral salts.—It is generally agreed that the action of these compounds in the dye-bath is of a physical nature. It is assumed that the decreased solubility of the direct dyes in saline solutions is the chief cause of their action. This may be so, but little work has been done on this subject to prove it. If this were the only action, it is clear that in any solution the cotton fibre should dry a darker colour in the cold, for the dye would be still more insoluble under these conditions.

In practice the reverse is the case. The fibre state is clearly an important factor, and here temperature is possibly more important than the decreased solubility of the dye under any working conditions.

Under constant conditions of temperature, &c., a carefully conducted series of experiments, dealing with the relative solubilities of these direct dyes and their dyeing actions in, say, solutions of sodium sulphate of different strengths is required; also the relative actions of the different assistants of this nature, as compared with their influence on the solubilities of the dyes, the solubility tests to be made at the temperature of dyeing.

A series of figures (W. M. Gardner, *Text. Manuf.*, 1890, 345) has been given indicating the best proportions of salt to add to the bath to get the maximum effect. The conditions of the trials are of too indefinite a nature to be of much value from a theoretical point of view.

The experiments suggested above might be extended. Skeins dyed with colour should be boiled with white skeins in different saline solutions and the relative rates of diffusion compared, the relative solubilities under the conditions of the experiments being carefully noted. The writer hopes to give this subject attention.

There is nothing which more clearly indicates the indefinite nature of our present knowledge of the subject of dyeing, than the absence of reliable information on the action of these bodies, especially when we consider their great value, and general use in dyeing.

It is hoped that before long these interesting problems will be cleared up.

Reference may be made to the experiments of Hallitt on the action of sodium sulphate in the dyeing of wool, which, for convenience, is noticed elsewhere.

The action of formaldehyde on the fibre substances, and the influence of this body on the general process of dyeing are characteristic, and a further examination in this direction is needed.

The coagulating action of the substance on albumin and gelatin is well known. In a similar way, wool, and silk fibres are influenced by this reagent.

The keratin of the wool fibre is rendered less soluble. Beyond becoming harder the wool suffers little from this treatment. It is much more resistant to change in the presence of alkaline liquors, and steaming, or boiling in water, has less disturbing influence on the fibre.

The treatment is, therefore, of advantage where wool is dyed with the sulphide dyes.

In the same way the silk gum present in raw silk may be rendered less soluble under the action of alkaline liquids, and soap solution.

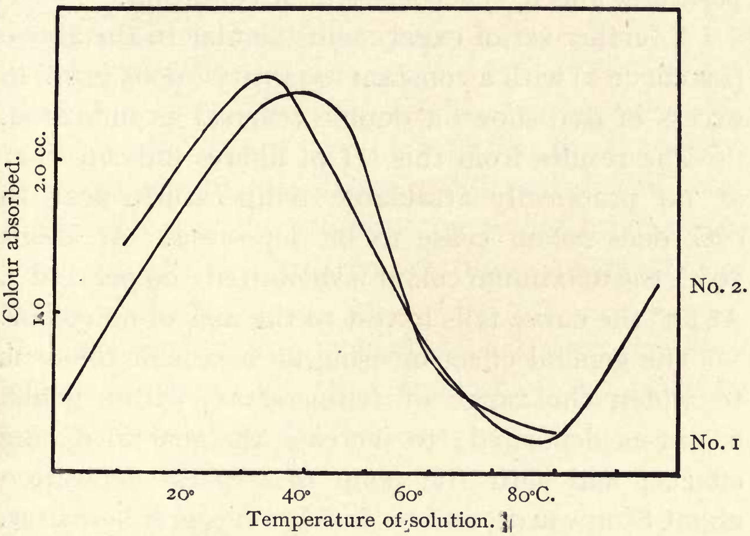
This reagent is used to fix direct blacks on cotton. In this case the application follows the actual dyeing, and takes place at a temperature of about 160°F.

J. Collingwood (*J.S.D. and C.*, 1905, 243) shows that with Diamine, Columbia and Zambezi Blacks the effect of treating in this way is to increase the fastness to acids and washing. The fastness to light is not appreciably altered.

The dyeing of basic colours on cotton treated with casein followed by formaldehyde is of interest.

The baths are said to be exhausted, and the shades bright and good.

The *Influence of Temperature on Dye Absorption* is indicated in the following curves.



ROSANILINE ACETATE ON WOOL.

(OH_2 ·200 cc. : Dye solution ·1 grm. per litre : Wool ·5 grms.)

The reversal in the absorption of the dye as indicated in the curve is attributed to dissociation stress, which is said to take place at high temperatures with this dye.

Assuming Hood's law, and considering the absorption as due to chemical effect, as well as the dissociation of the rosaniline acetate, the combined effect should be proportional to the fourth power of the temperature.

The sum of the fifth differences being only – .07, or very nearly zero, and this being also a criterion of a quadratic curve, the equation of the curve is

$$y = b\,(t + 1.46) - c\,(t + 1.46)^2 - d\,(t + 1.46)^3 + e(t + 1.46)^4$$

when y is amount of colour absorbed, t = temperature, and b, c, d constants of condition.

A further set of experiments similar to the above (*see* curve 2) with a constant quantity (.0005 grm.) in excess of dye shows a double reversal as indicated.

The results from this set of figures indicate that at no practically attainable temperature, near to 0°C. does colour cease to be deposited. At about 39°C. the maximum colour is deposited (.09 per cent.). At 82° the curve falls lowest to the axis of no colour.

The general effect of using an excess of colour is to widen the range of temperature, within which colour is deposited; to increase the general dyeing effects; and shift the point of greatest deposition about 8° upwards, and to doubly reverse it hereafter.

With mauveine the calculated point at which no colour would be taken up is – 23.8°C. At 49° there is greatest deposition of colour (.08 per cent.). Then there ensues a single inflexion in the curve, and lastly, the curve descends rapidly to the axis of no colour, although at 85°C. it is still remote therefrom.

The positive disadvantage of dyeing with these basic colours at high temperatures is therefore apparent, so far as colour absorption is concerned.

The absorption of dyes by wool has also been studied by Brown (*J.S.D. and C.*, 17, 92).

The dye left in the solution on 100 parts taken is shown for varying temperatures.

Dye.	20°	40°	60°	80°	100°
Acid Magenta . .	79	14	4	4·3	5·6
Tartrazine . .	46	3	1	1	·97
Indigo Carmine .	46	3	3·4	3·5	6.2
Acid Green . .	79	18	4	3·6	5·2
Acid Violet 4 BW. .	44	26	20.8	20.8	28.7

These variations are of interest to the dyer. They indicate the possibility of different shades being produced by a dye solution containing mixtures of these dyes at different temperatures, irrespective of depth of shade.

They explain also why in wool dyeing the fibre will often absorb a further amount of dye, if left to cool in the dye solution.

CHAPTER VI

SOLUTION AND THE PROPERTIES OF COLLOIDS

At every turn the dyer is brought in contact with solutions of dyes, mordants, and other substances; and it is therefore necessary for him to have some idea as to the physical state of substances in solution.

Many of the difficulties met with in the dyehouse are intimately connected with the solution state of these materials.

In cases where the remedies take the form of alteration in the strength, or temperature of the dye liquors; or the addition of third substances to the same, the changes brought about in the dyeing processes are clearly due to corresponding variations in the solutions themselves. Through these the absorption of the dyes may be modified, and different dyeing effects produced.

This subject, generally, is a complicated and involved one, and has given rise to much controversy.

A general clearing up of our ideas on the subject is urgently needed, in view of the importance of its influence on many branches of physical chemistry.

The solution state of a dissolved substance may, if the ideas of to-day are correct, be ascribed to one of two actions. It may be that both are involved in the production of solutions.

Stated briefly, the molecules of the dissolved substance (solute) are either in association with the solvent molecules; or else they simply migrate in an inert solvent, or medium.

The issue is therefore clear and defined.

In the latter case the solute is considered to be more or less in a state of dissociation, being split up into ions which also have the power of independent migration in the solvents, the cause of this action being unknown.

The two theories may be termed the association, and dissociation ones respectively. They may be said to include all the possible explanations of these phenomena known to us at the present time.

The association theory was primarily based on the work done by Mendeleef on the isolation of definite hydrates in solutions. The work of Crompton and Pickering supported this view. Prof. Armstrong in this country, and H. C. Jones in America, have advocated this conception of solution.

The original idea of Mendeleef supposes, that a series of hydrates are formed in the aqueous solution; and that these hydrates are in equilibrium with the solvent and with one another. It must be remembered that the presence of such compounds has not been recognised in the case of many other solvents, but a number of hydrates have been isolated by crystallisation from aqueous solutions by the above investigators; and many others have been indicated by the alteration in the physical constants of the solutions.

Armstrong suggested that the association was only between the solvent molecules and the negative radicle of the solute only.

In dealing with the phenomena of pseudo solution and de-solution in dye solutions (*J.S.C.I.*, 1905, 228), I ventured to suggest that the action might be of an intermediate nature, it being assumed that the so-called secondary attraction of the solvent molecules for those of the solute *correspondingly* reduces the primary attraction between the positive and negative radicles thus:

$$(OH_2)_x \ldots H\text{—}Cl \ldots (OH_2)_x$$

As a result the hydrogen and chlorine atoms are never entirely beyond the influence of their primary attraction for one another. Their mutual influence is lessened, but not entirely replaced by the secondary attraction.

On the other hand, Dr. Lowry has more recently advanced the hypothesis that actual dissociation may occur owing to the formation of "hydrated" ions. For instance, he represents the solution of potassium chloride as follows:

$$\overset{+}{K}.(H_2O)_x \qquad \overset{-}{Cl}(H_2O)_x.$$

The solution state, so far as the solute is ionised, is represented as split up into ionic hydrates. The full argument in favour of this theory is set forth in a recent paper read before the Faraday Society.

So that we have the three possible states of solution, the ionic, the associated, and the intermediate one, which assumes that the primary and secondary attraction are interchangeable and of the same order.

There is a further and alternative hypothesis, which associates the action in the case of aqueous solution with the presence of an unsaturated tervalent oxygen atom.

The subject is, therefore, narrowed down, so far as our ideas extend at the present time, as indicated. Enough is already known to enable us to judge the importance of the whole subject. It is impossible, however, at the present time to indicate the hypothesis which will be ultimately accepted as most truly representing the solution state. In the meantime the dyer cannot fail to gain information on the condition of his solutions, and their possible actions, by keeping in touch with the general principles laid down from time to time in connection with this subject.

It may be generally stated that all substances are soluble in water. There is apparently no exception to this rule. Even such substances as quartz, platinum, and gold, are soluble. It may be accepted as a fact, therefore, that no known substance is able to withstand the solvent action of water. The degree of solution varies; sodium sulphate is very soluble, barium sulphate is relatively very insoluble.

Yet the solvent action is there; the general action is the same in both cases.

When, therefore, water is brought into contact with any substance, fibres, dyes, salts, copper vessels, &c., solution takes place in every case. Although this action may in some cases be neglected, yet, under certain favourable conditions it may adversely influence the dyeing results. This solvent action may be greatly modified by the presence of third substances, such as acids, or alkalies, and must be carefully considered.

As previously stated, the dissociation theory assumes that salts, acids, and bases are more or less split up into electrically charged ions on dissolving in water.

According to Faraday's law, hydrogen and the metallic radicles are positively charged, while hydroxyl and radicles are negatively charged.

Acids in aqueous solutions are supposed to act as such by virtue of the free hydrogen ions present. Consequently the hydrogen ions in a given equivalent of acid are said to determine its strength as an acid.

These H ions are also supposed to have the power of carrying electricity, and consequently the more free ions present the greater will be the carrying power, or conductivity of the solution.

Beyond a certain stage of aqueous dilution Kohlrausch found that the molecular conductivity of these substances reached a maximum value.

The dissociation theory implies that at this point the substance is entirely split up into ions, or, in other words, completely dissociated.

Having therefore determined the molecular conductivity of an acid at infinite dilution (that is to say, at the point of maximum dissociation), its molecular conductivity at any other dilution greater than that will vary as the number of ions present.

So that the ratio of the molecular conductivity at any dilution v to the molecular conductivity at infinite dilution will give the degree of dissociation at any other dilution thus :

$$\frac{\mathrm{U}v}{\mathrm{U}\infty} = \mathrm{M}.$$

The future investigations on the action of dyeing will certainly be closely connected with the abnormal actions of substances in the colloid state. When the nature of the fibres and dyes is considered, it will be seen that every dyer should have at least an elementary knowledge of the properties and actions of these bodies.

The further study of this subject must undoubtedly lead to important results. Whether the advanced views held by some investigators will be ultimately accepted, or not, is hardly a fit subject for speculation. The study of these substances, their properties, and their relations to other materials with which they may be brought into contact, is a wide one; and many years will probably elapse before our knowledge is brought down to anything like a firm or satisfactory basis.

Be this as it may, sufficient facts have already come to light to lead us greatly to modify our views and theories, and undoubtedly this disturbing influence will tend to become greater rather than to decrease.

Not the least important result of these investigations will certainly be directly to influence our ideas on the so-called ionic theory of solution. It may be that they will lead to its destruction or they may possibly add additional, and perhaps it may be said, much-wanted confirmation of the general principles laid down by those who support, and uphold it against an increasing number of opposing facts. At any rate, the study of colloids when in a state of pseudo-solution cannot fail to indicate fresh lines of research, which may, in their general effect, help us to understand many points which are at present beyond our range of thought, and experience.

It is here also, that the true relations between dyeing and physical chemistry will become evident.

There is little doubt but that many actions which are of but everyday interest to the dyer, and at present almost beneath the consideration of the physicist, will be ultimately recognised as of prime importance, and lead to a general extension of knowledge.

A rapid survey of the actions which make up this most useful art will make this at once evident. The extreme delicacy of the colour reactions, the nature of the dyes, the extreme complexity of the problem, which deals with the ultimate determination of the fibre-state, and all that this entails, indicate that the future study of this subject cannot but have its direct influence on the general considerations upon which we shall ultimately base our knowledge and theoretical speculations on the state of matter, and the forces which influence it.

Graham divided all substances into two classes, viz., crystalloids and amorphous substances (colloids). We already know that this division is of an arbitrary nature; but in the absence of a direct method of accurately determining the condition of the state taken up by these units in solution, as regards the exact condition of the dissolved substance, we are unable at present to do much more than indicate that this division, like so many others which were set up during the nineteenth century, is not altogether a satisfactory one.

Crystalloids undoubtedly, when dissolved in, say, water, change its physical properties to a marked degree. They diminish the vapour tension, lower the freezing-point, and raise the boiling-point. In fact, they act as if there exists a more or less close relationship between the molecules of the solution and the solute, which modifies the normal properties of the solvent liquid.

On the other hand, the so-called colloids do not seem to enter into so close a relationship with the solution system, and this seems to be confirmed by the fact that the molecules of the latter seem to be present in a state of higher aggregation.

Correspondingly, they exert little influence on the state of the solvent, for they do not materially alter its freezing- or boiling-point or the vapour tension.

These bodies are therefore regarded more in the light of mixtures, or suspensions than true solutions.

But all these divisions are of an arbitrary nature, and only serve as stepping-stones on our way to a serviceable appreciation of the true facts of the case. They are crude, and must never be accepted as anything more than the scaffolding, which will ultimately be removed when our knowledge is more complete.

Although in some ways the relationship between the solution and solute seems to indicate that colloids do not enter into such close relationship with the solution, yet it must not be lost sight of that they persistently retain what we call "water of hydration." This, taken in conjunction with the above facts, will indicate the extreme complexity of the reactions which govern the relative relations between the two systems,

(Solution + crystalloid) and (solution + colloid),

and the impossibility of our natural division being anything more than a very incomplete and unsatisfactory one.

Colloids when mixed with water will generally form jellies when the proportion of colloid to water is within certain limits. In certain cases, the structure of these is so coarse that it may be visible to the eye under a low power objective. It is then seen to consist of a more or less solid framework through which the liquid is dispersed.

The two states in which a colloid can exist in a solution state, using this term in its widest sense, are termed the hydrosol state and hydrogel state respectively.

In its outward condition, the former resembles a true solution, such as a solution of sugar in water. The latter is of the nature of a jelly, and may be regarded as a two-phase state.

The dividing line between these two states is, in a way, a sharp one. It has been said that the critical point between them is as sharp as the crystallising point of an ordinary salt, but our knowledge of this alteration in the solution state when the one passes into the other is very indefinite. It is difficult to form anything like a mental picture of what goes on during the transition stage.

This idea of the solid framework through which the liquid is dispersed is perhaps the best, and only one, we have before us, which may indicate the fibre state of a silk filament at the time of dyeing. A similar state probably exists in the case of artificial silk under similar conditions.

In the case of other fibres our ideas of their construction will be modified from time to time, as our knowledge of their physical structure increases.

The crystalloids are capable of forming solutions which are perfect enough to pass through the interstices of these colloid jellies with considerable freedom. This very interesting fact must be carefully considered in its relation to the presence of these bodies in the dye solution, and their possible action in dyeing. As a matter of fact, the rate of diffusion of these bodies through gelatine or agar-agar is practically the same as that through pure water.

This was clearly pointed out by Voigtlander (*Zeit. f. Phys. Chem.*, 1889, 3, 316), who closely studied this question. The influence of temperature on the rate of diffusion is very marked. An increase in temperature will greatly increase the rate at which the salt will equalise itself over the whole solution system.

When the action of temperature on dyeing is considered, it will be seen that this action is one of special significance.

The following table indicates the relative rate of diffusion through agar-agar of some typical substances at different temperatures.

Substance	at 0°	at 20°	at 40°
Formic acid	.472	.867	1.49
Acetic acid	.318	.640	1.04
KHO	1.01	1.75	2.36
KCl	.786	1.40	2.18

On the other hand, the so-called colloids cannot pass through jellies or membranes except at very slow rates. It is only recently that it has been recognised that these bodies will pass at all. Dialysis, or the separation of colloids from crystalloids in their solutions is founded on this fact, and is a process in common use in chemical analysis.

The explanation of this action is obscure. Our knowledge of the subject is limited, and the possibility of colloids passing through membranes is one which deserves further attention.

Just as it is possible to prepare membranes which are permeable to water, but which will stop the passage of some salts (crystalloids), so at least some colloids are capable of slowly passing through certain membranes.

These semi-permeable membranes, which will stop the passage of crystalloids in some cases, are naturally closer in their structure than the ordinary ones. A porous pot holding in its structure a gelatinous precipitate of ferrocyanide of copper will act in this way. (*Proc. Chem. Soc.*, lix. 344.)

It is interesting as a matter of history to note that this passage of liquids through films (parchment paper, bladders, &c.,) which is called osmosis, was first noticed by Abbé Nollet in 1748.

It may be here mentioned, and it is pointed out in fuller detail elsewhere, that in considering the cause of this action which leads to diffusion it is not sufficient to assume that the size of the aggregates in solution is the only controlling factor.

The author has attempted to explain the slow dialysis of colloids by assuming that molecular migration takes place in pseudo solutions from one aggregate to the other.

This idea of molecular migration in pseudo solutions is founded by analogy, on the Poisson theory of atomic migration. It offers a possible explanation of the mechanism of the dialysis of colloids (Dreaper, *J.S.C.I.*, xxiv. 223, and *J.S.D. and C.*, May 1905).

This migration of the individual molecules from one complex to another may explain the slow dyeing action, or absorption of lakes like those of alizarine by the one-bath method, where the so-called molecular weight of the aggregates is a high one; the "levelling up" action in dyeing; the passing of a solution of gun-cotton through a membrane; and the slow "ripening" of solutions of cellulose, or its compounds, in the manufacture of artificial silk.

By assuming this action, it is possible to explain the slow passage of large aggregates through a membrane, or "sieve," where the direct passage is prohibited by size.

An alternative explanation given by Prof. Ramsay (*J.S.C.I.*, 1904, 296) is, that the cotton molecules may become deformed in shape, and glide through the interstices of the membrane like worms.

If a solution of a crystalloid be separated by a porous membrane from pure water, certain so-called osmotic phenomena are set up, and enormous pressures may result from this action.

This osmotic pressure may be measured directly, or, more easily calculated. In the case of mineral acids and salts the actual pressure is in excess of the calculated results. From certain theoretical conclusions Arrhenius accounts for this by assuming the dissociation of the acid, or salt. In this way the number of individual units in solution is increased, and with it the pressure, or osmotic effect.

There is no generally accepted view as to the cause of osmotic pressure.

The dissociation theory assumes that the dissolved substance exists in the solution in a state, so far equivalent to a perfect gas, that it obeys laws, which are similar to those governing the latter.

The association theory, on the other hand, assumes some attractive force at, work which forms aggregates consisting of solvent and solute molecules. At any rate, the phenomena of osmosis are directly connected with the state of the solution at the time they are exhibited, varying with the condition of the solute, and its solution state. Action at the surfaces of the membrane also seems to play an important part in these phenomena.

The absorption of water by colloids is clearly of the first importance to the dyer. The preliminary operations to dyeing, apart from the question of the colour and gloss of the fibre, and its condition during the mechanical stages of its manufacture, are chiefly connected with the object of presenting the fibre in a uniform condition to the dye-bath. All foreign substances of a nature which will defeat this end, such as wax, grease, &c., are as far as possible removed by alkaline, or other treatment. The thorough wetting out of the fibre before it is brought into the presence of mordant, or dye, is also well understood, and its need cannot be over-estimated.

From the theoretical point of view, all these operations are conducted with the object of equally permeating the fibre substance with the aqueous solutions. The result of this is to obtain a fibre condition, corresponding more, or less, to the so-called hydrogel state and as far as possible an equal state of hydration.

A study of the way in which silicic acid gives up its water of hydration indicates the state in which it is held. The elimination of water by this hydrogel is a gradual and continuous one, decreasing as the anhydrous state is reached (Bemmelen, *Zeit. Anorg. Chem.*, 13, 233).

The influence of these hydrogels on the properties of the "solvent" is small.

The colloids exert little or no influence on osmotic pressure, boiling-point, freezing-point, or electrical conductivity of the solution, and in this way differ entirely from crystalloids.

It has been shown that solutions of these colloids may be made to gelatinise, or enter the hydrogel state, by the addition of small quantities of certain substances. This action is different to that shown when a crystalloid is made to partly leave the soluble state in a supersaturated solution, by the addition of a crystal, or other substance. It is only local in its effect in the case of colloids.

The hydrogels have undoubtedly the power of absorbing foreign substances in solution. For instance, metastannic acid readily absorbs hydrochloric acid, or sodium sulphate, and, probably, many other substances (Bemmelen and Klobbie, *Zeit. Anorg. Chem.*, 23, 111). The concentration of the hydrochloric acid was often found to be greater than in the solution. The absorption factor

$$K = \text{conc. in colloid} \, / \, \text{conc. in } H_2O,$$

is not a constant in this case, but is dependent on the concentration at the point of equilibrium.

A further point is that the absorption of substances is *proportional to the hydration of the colloid.* This is of the greatest interest from the dyer's point of view. It is found that silicic acid absorbs compounds in the ratio of its state of hydration (Bemmelen, *J. fur Chem.*, 23, 324). Similar interesting results were also obtained with SnO_2 in different states of hydration.

$SnO_2.2.3H_2O$ absorbed more acid than $SnO_2.1.2\ H_2O$.

When we consider the conditions of the fibres which give the best dyeing results, so far as dye absorption is concerned, it will at once be seen how closely they approximate to those which give the highest absorption results in the cases of inorganic hydrogels given above.

The importance also of an equal state of hydration from the dyeing point of view is clear when we remember that it is very desirable to obtain an even shade, or absorption of dye. This is a necessary condition so far as piece or yarn dyeing is concerned, in practically all cases, although not so necessary in dyeing loose wool, or cotton.

So that the condition of the fibre at the time of dyeing is of the first importance, and probably the conditions of the dye solution are unconsciously arranged or determined by the dyer as much with the object of obtaining a correct fibre condition, as modifying the physical (or chemical) state of the dye solution. The dyer must recognise the possible and variable action of the fibre as well as the dye-stuff, when the conditions of dyeing are altered.

Hydrogels, particularly those of the dioxides of silicon, tin, magnesium, &c., can form absorption compounds with gases and liquids, and are able by absorption to remove acids, bases, salts, &c., from solutions in which they are placed.

This action goes on until a state of equilibrium is established. The state of equilibrium alters under changed conditions of temperature, strength of solution and amount of liquid per unit of hydrogel.

The principal phenomena of absorption have been described as follows (Bemmelen, *Landw. Versuchs. Stat.*, 35, 69):

(1) When an absorbent substance gains, or loses some of the absorbed substance, in all probability each particle becomes equally richer, or poorer, in the absorbed substance. In this way they differ from chemical compounds. When the latter suffer dissociation a certain number of molecules are completely decomposed, and the rest remain intact.

(2) The power of absorption is not constant, but varies as the action goes on. The attraction for the first portion is strong. As more is absorbed the tendency to absorb decreases rapidly. The action takes place more slowly. In the same way the latter portion is given up more readily to solutions.

(3) The absorptive power of colloids varies with their method of production, and the subsequent treatment they are exposed to.

(4) Hydrogels may change into ordinary chemical hydrates acquiring a definite composition, and even a crystalline form. In doing so they lose the power of forming absorption compounds.

It would seem, therefore, that at, say, a higher temperature the residual chemical attraction is more definitely confined to the hydrate complex.

This is indicated also in the fact that the formation of a colloid compound is accompanied by the evolution of considerably less heat than is evolved in the formation of the corresponding crystalline form.

(5) Increase of temperature affects the absorptive power. It sets free a certain amount of water from the hydrogel, and also increases the solvent action of the water, or the substance absorbed.

Consequently the rate of absorption decreases.

(6) Every hydrogel has its own specific rate of absorption for each acid, base, or salt. One hydrogel may absorb acids more powerfully than it does other substances, another one will absorb bases more powerfully, and another salts. In general, absorption is strongest when under the circumstances the hydrogel, and the absorbed compound can combine chemically. An example of this action is seen in the case of stannic acid. This absorbs a good deal of sulphuric acid, but much more potash. (*a*) The substance dissolved may be proportionately divided between the water of the hydrogel and the water of the solution, as in the case where potassium chloride is absorbed by the hydrogel of silica.

(*b*) The hydrogel may absorb a larger proportion of the dissolved substance. The hydrogel of metastannic acid will absorb nearly all the potash from a solution.

This absorption may even cause decomposition of the dissolved substance. The hydrogel of silica will remove potash from potassium carbonate, or soda from disodium phosphate. On shaking up the same hydrogel with calcium carbonate and potassium chloride, there is an absorption of lime and potash, and a corresponding amount of calcium chloride and calcium bicarbonate remains in solution. Some potassium chloride is also absorbed.

(7) The condition of the hydrogel and its weight being given, the temperature also being known and remaining constant, and the hydrogel not being soluble in the solution, the amount of a particular substance absorbed by it varies with the state of concentration, and with the amount of solution.

A state of equilibrium is established between the absorptive action of the hydrogel on the one hand, and the opposing action of the water on the other. If chemical decomposition also takes place, the attraction of chemical combination takes part in producing the equilibrium.

The stronger the solution the more of the substance is absorbed, but in decreasing quantity. The limit is reached when after the equilibrium is established the liquid is in a saturated condition. No satisfactory formula can be obtained to represent the action generally, except in very dilute solutions, and where the absorptive power of the colloid is weak, when the curve obtained is practically a straight line.

(8) One crystalloid absorbed by a hydrogel may be replaced by another.

If a hydrogel which has absorbed A be placed in a solution of a substance B, then the solvent will dissolve out some of A, and at the same time some of B will be absorbed until equilibrium is established, but no true substitution takes place.

If the absorption quantities are small, A and B are absorbed without mutually influencing one other to a noticeable extent. If the quantities of A be large, there may be a loss by substitution.

The last part of A absorbed, which is not held so strongly, may be replaced by B.

It has been noticed, however, that by repeatedly treating the hydrogel with solutions of B, the latter may entirely replace A. In the event of chemical action taking place between A and B in solution, the action may be greatly complicated, and even entirely altered.

The ultimate absorption of the substance by the hydrogel depends entirely upon the final state of the solution.

An important statement has been made by J. Billitzer (*Zeit. Phys. Chem.*, 1903, 45, 307), as a result of some experiments on the " carrying down " of calcium, chromium, sodium and potassium chlorides when they precipitate colloids. The fact seems to be established that they act in the ratio of their chemical equivalents in their precipitating action.

If potassium chloride is used as the precipitating electrolyte, acid is set free when the colloid is electronegative; on the other hand, when the colloid substance is electropositive alkali is liberated.

The colloids may be divided into two classes, according to their action, when under the influence of a high E.M.F., and may be classified into electropositive and electro-negative units, as the case may be.

The electro-negatively charged particles move to the anode, and the electro-positive ones to the cathode.

Colloids, or suspensions, which are charged in opposite directions will precipitate each other if present in certain proportions.

Aniline dyes act as colloids in this respect. The acid dyes were found to migrate towards the anode and the basic dyes towards the cathode (Neisser and Friedemann, *Chem. Centr*, 1904, 1, 1387).

The coagulating effect produced on solutions of colloids by reagents is of a complicated nature. It does not seem possible to give any definite reason for their action. We must content ourselves with the recorded facts which in themselves seem very contradictory; they at least indicate the very complex nature of the phenomena before us.

The one thing which seems certain is that electrolytes, or soluble salts, have the power of degrading hydrosols into hydrogels, and that in doing so the precipitating reagent may be partly, or wholly, precipitated at the same time. It must, however, be remembered that other substances will also precipitate colloids. That this action may be of a mechanical nature is seen in the fact that if barium sulphate is shaken up with some hydrosols, it will carry down with it a good deal of the colloid substance.

In other cases, we may have a soluble salt acting in this way, and being decomposed in the process.

J. Duclaux (*Compt. rend.*, 1904, 138, 571) affirms that the precipitated colloid usually contains a certain amount of one of the radicles of the salt used to produce coagulation, the change being produced by simple substitution of one of its radicles for an equivalent amount of one of the constituents of the colloidal substance. The solution after coagulation will contain a small amount of the radicle displaced from the colloid. Linder and Picton's recent work seems to support this.

It seems that in the neighbourhood of the coagulating point a slight change in equilibrium will produce a much larger visible effect on the colloid, so that the latter is easily precipitated.

The precipitation of proteid substances by acids, copper, or silver salts is in each case a reversible one, the precipitate dissolving in excess of the reagent. (V. Henri and A. Meyer, *Compt. Rend.*, 1904, 138, 757.) This is a reaction which it will be advisable to keep before us in the study of the action of mordants and dyes. It may be possible to explain certain reactions in this way, which at present are more or less obscure.

It would follow that the composition of the fibre might be expected to have a great influence on the results produced in different cases.

All inorganic colloids seem to be more or less absorbed by cotton, wool, or silk fibres. This is stated to be quite independent of the chemical nature of the dissolved colloid. (W. Biltz, *Ber.*, 1904, 37, 1766.)

It is, perhaps, not safe to argue from the inorganic to the organic colloids so far as their general reactions are concerned, for the inorganic colloids seem, at best, to be present in a very degraded state in their solutions. As has before been pointed out, they may be carried down in a mechanical way by such rough suspensions as barium carbonate, and are then firmly held against resolution. Organic colloids such as dyes are not so readily carried down, or held, in this way.

In passing it is interesting to note that the method of precipitation of insoluble salts in colloids like gelatine, is of an irregular nature, so far as distribution is concerned. Liesegang noticed, for instance, that silver chromate precipitated *in situ* (in capillary tubes) by the diffusion of silver nitrate solution into gelatine in which potassium chromate has been dissolved, gives rise to unequal precipitation. The silver chromate occurs in laminæ at right angles to the direction of the tube.

The relative condition-state of hydrosols and hydrogels so far as is known, is as follows. The two states seem to be in a way, distinct, that is to say, there is generally a critical point in the passage from one state to the other which corresponds, in a rough way, with the difference between the solid and liquid state in ordinary substances. This statement must only be taken in a general sense. Further knowledge may indicate that the dividing line is an imaginary one, but for practical purposes we may consider the two states as distinct. Taking the hydrogel state as consisting of a framework, more or less perfectly developed, as the case may be, permeated by a liquid, it may be said to be a two-phase system—the framework or more insoluble portion corresponding with the solid phase, and the other with the solution state. In this gelatinised state the water may be partly held by capillary action. The power with which colloids will take up moisture is immense. The molecular forces which come into play when colloids lose water are correspondingly great. Gelatine on drying will strip off the surface of a containing glass vessel.

The rate at which chemical action may take place in colloid solutions is not altered to any great extent.

The classification of the colloids is evidently impossible at present. It has been proposed to divide them roughly into two classes, having respectively a molecular weight either above or below 20,000. In the former we find starch (25,000), silicic acid (49,000), and in the latter would come tannin, dextrin, ferric hydroxide (6000).

It would seem that it is the colloids of higher molecular weight which give non-reversible solutions on freezing. (Linnebarger, *J. Am. Chem. Soc.* 20, 1898, 375.)

Such proposed methods of separation as that of shaking up the solution with barium sulphate hardly deserve attention.

Until we more thoroughly realise the state in which colloids exist in pseudo solutions, it will be impossible to derive any satisfactory method of classification.

There is need for a standard of solution, and a ready method of comparison with other states. This may either take the form of a standard solution, or a calibrated porous partition for diffusion experiments.

A colloid which seems dry to the touch (such as gelatine or silk) contains a considerable amount of water, which it may lose on further drying at a temperature of 100° C., the state of the fibre continually changing with its composition. This action, at ordinary temperature, may be a reversible one. If a colloid be dried so that its vapour tension is nil, it may regain its water partially, or entirely, on exposure to the air. This will depend on the complete reversibility of the process, and will vary with different substances and conditions.

In a closed space partially saturated with moisture, a colloid loses water until its vapour tension is equal to that of the surrounding medium.

The rapidity of dehydration constantly diminishes until it reaches a minimum as the vapour tension approaches that of the enclosed air. For example, colloidal metastannic acid containing 2.2 mols. of water lost .55 mols. the first day. The quantity lost decreased gradually, until on the 13th day only .01 mol. per day was lost, and the composition was .79 mol. OH_2. (Bemmelen, *Rec. Trav. Chim.*, 7, 37.)

When this process of " hydration " becomes non-reversible, which happens when most colloids lose water, especially when drying at a high temperature complicates the action, the non-reversible modifications have a diminished absorptive power, but at the same time they retain their water with more energy. This is an indication that the secondary chemical action involved may be constant in its amount, varying in intensity with the ratio of colloid to water. In the transformation of a colloid into a true hydrate a state of equilibrium is reached with fewer molecules of water, with the formation of correspondingly larger aggregates. It may undergo modification at a suitable temperature, so that it becomes insoluble in the medium in which it was originally dissolved.

Colloidal silica will hold more water at 50°, or even at 100°, in a medium saturated with aqueous vapour, than at 15° in dry air. (*Ibid. Rec. Trav. Chim.*, 7, 69.)

The precipitating action of salts on colloids seems to be a general one.

The idea has been put forward that the precipitating action of colloids is a dehydrating one. Tomasso, (*Compt. Rendus*, 99, 37) does not agree with this, some salts, it being held, acting in the opposite direction. Sodium acetate, sodium sulphate, potassium bromide, and potassium chlorate are said to act by retarding the dehydration of cupric hydroxide into copper oxide. On the other hand, potassium chloride and sodium carbonate act in the reverse direction.

All proteids (except peptone) are precipitated by a neutral solution of ammonium sulphate. All colloids seem to act in this way, including soap, soluble carbohydrates, glycogen, &c. (Nasso, *Pflüger's Archiv.* 41, 504.)

This writer will not allow, however, that the cause of the precipitation is due to the struggle for water which takes place between the colloid and the salt. A series of experiments tend to show that this is not sufficient to explain the results obtained.

The presence of a salt is not necessary to precipitate the colloids. Plaff, Geiger, and Payen have shown that separation may take place by freezing in some cases. A colloidal solution of antimony trisulphide (Schultz's method) is entirely separated by freezing. On the other hand, albumen is not separated, or, if it is, the action is a reversible one. (Lubavin, *J. Russ. Chem. Soc.*, 21, 397.)

The reduction of the freezing-point of water by colloids is very slight. This indicates very high figures for the molecular weights.

Gallic and tannic acids are said by Paterno (*Zeit. Phys. Chem.* 4, 457) to show a very high molecular weight. When dissolved in acetic acid they are said to give normal results. This is, however, denied by Sabanéeff (*J. Rus. Chem. Soc.*, 22, 102).

The state of egg albumen (15 per cent. sol.) is said by this investigator to correspond with a molecular weight of 15,000.

On the other hand, Gladstone and Hibbert (*Phil. Mag.*, 26, 38) obtained results by Raoult's method, which indicate a molecular weight of 2000.

Guthrie's original statement that colloids do not influence the boiling-point (or freezing-point) of water, or in other words, that the tension of aqueous vapour of solutions of colloids equals that of water, is not correct. Gelatine, for instance, is said to raise the boiling-point.

The student is referred to the work done by Morris (*Trans. Chem. Soc.* 1888, 610, and 1889, 466), which indirectly is of interest to those engaged in the study of the absorption of dyes.

Hydrolysis in solution certainly seems to take place in many cases. For example, potassium cyanide is partially decomposed into KHO and HCN in aqueous solution (Shields, *Phil. Mag.*, (5) 35, 365). The action of water in producing this effect is called hydrolysis.

Probably all salts are hydrolysed in aqueous solution, but in many cases to an exceedingly small extent.

Esters as well as salts are hydrolysed. Methyl and ethyl acetates are decomposed into acetic acid and the corresponding alcohol. The extent to which hydrolysis takes place is regulated by mass action.

Veley (*J.C.S.*, 1905, 26) considers that the decomposition of ammonium salts on boiling is due to hydrolysis, and not dissociation.

The cases where hydrolysis is possible are said to be:

(1) Salts from weak bases and strong acids.

(2) Salts from strong base and weak acid.

(3) Salts from weak base and weak acid.

It would therefore seem to be a function of an unequal atomic bond, and this confirms the above theory of association rather than dissociation, when the actual reaction between the water molecules and the solute is considered. For instance,

$$KCN + H_2O \rightleftarrows HCN + KHO.$$

The laws for electrical conductivity in the above cases are stated to be

$$(1) \quad \frac{C\ (\text{acid}) \times C\ (\text{base})}{C\ (\text{salt})} = K.$$

and in the case of (3)

$$\frac{C\ (\text{acid}) \times C\ (\text{base})}{C^2\ (\text{salt})} = K.$$

In (1) the amount of the action is stated to depend on dilution. In (2) it is independent of dilution beyond a certain limiting value. In (3) hydrolysis is nil, or inappreciable.*

The influence of the dissociation of dyes in solution has been discussed by Vignon (*Bull. Soc. Ind. de Mulh.* 1893, 407 and *J.S.D. and C.* 1893, 44).

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* For further information on this subject the following may be consulted—Walker: *Zeit. Phys. Chem.*, 1889, 4, 319; Arrhenius (*ibid.*) 1894, 13, 407, and Van't Hoff, *Chemische Dynamik*, (1898) 121–126.

From this point of view the three factors influencing the action of dyeing would be:

(1) The absorbent fibre;
(2) The dye-stuff;
(3) The solvent;

an equilibrium being established and determined by chemical forces, and the conditions of dissociation, resulting in any case in the dye effect observed.

This matter has been further studied in greater detail by Knecht (*J.S.D. and C.* 1898, 59; 1903, 158; 1904, 59).

Diamine sky blue, for instance, is said to dissociate quite as readily as any basic dye, when tested by the filter-paper method.

On the other hand, the sulphonated basic dyes like acid green, or acid violet, show no dissociation by the above test. These results are said to correspond very closely with the dyeing effects of these dyes on wool. The alcoholic solutions of these dyes do not show dissociation by this test. They have also no dyeing power on wool. It will be noticed, however, that the possible difference in the action of alcohol and water on the fibres themselves is disregarded.

The halo formed on paper by this method with magenta can be prevented if hydrochloric acid is present in the free state. Correspondingly, wool will not dye in the same acid solution of the dye, and this reagent may act by preventing the dissociation effect in both cases.

Acid colours will show this separation of the colour acid (on acidifying the dye solution), but as a general rule they will give no halo in neutral solutions.

The colour acids are insoluble when compared with their sodium salts. They are, therefore, probably in a state of high aggregation, and in this molecular condition would be more under the influence of surface action. This must not be overlooked.

It will be noticed that the influence of the solution state on the rate of dyeing may be a very important factor. Dyes may be attracted by the fibres from some solutions, and not from others. They may also be removed from the fibre in some cases by the second solvent, in which they are more soluble.

That the presence of moisture is necessary in order that the action may be complete seems to be confirmed by the recorded fact that better results are obtained by the use of very moist steam in fixing direct cotton dyes on cotton after printing. (*Wilhelm, Proc. Soc. Ind. de Mulh.* 1904.) The dyes would seem to require a certain amount of steam (moisture) to fix them under these conditions.

The exact cause of this action is unknown. The increased hydration of the fibre may play some part in the reaction.

Some experiments on the absorption of rhodamine base from solution in benzene are also of interest (Weber, *Farb. Zeit.* 1899, 1). They indicate that a highly hydrated fibre state is not necessary for the "dyeing" to take place in this case. Cotton fibre will absorb the base from this solution, but the resulting shade is not very fast against washing, indicating that it is imperfectly fixed in the fibre substance.

In the same way, precipitated cellulose, which is in a more highly hydrated form, will dye more readily than the original cotton with some dyes. They are also faster against washing. It must be remembered in connection with this subject that mercerised cotton will give a darker shade with the same percentage of dye.

It may be argued that the increased absorption is due to the greater number of OH groups present in the cellulose molecule, or aggregate. In connection with this it may be noted that the cellulose tetracetate, which is very resistant to any ordinary hydrating action of water, as tested by its physical properties, will not take up dyes under these conditions.

It has been stated that alizarine lakes, which are soluble in alcohol-ether, are readily dyed on cotton from such a solution. If this is so, the matter is one of interest, on which the writer hopes to give further details later. It is difficult to see how dyeing can be due to chemical action in this case.

It is possible that light may be thrown on the subject of the colloid state by the study of the mutual solubility of liquids. J. P. Kuenen (*Phil. Mag.* 6, 1903, 651) expresses the opinion that in these mixtures and at the point of saturation, the molecular conditions set up, which may probably be represented by a high molecular attraction, make it impossible for the solvent to dissolve more than a limited amount of the solute, or second substance, without entering upon an unstable condition. If this is so with partially miscible liquids, the same should apply to pseudo-solutions. Beyond the point of saturation the solute will be in a state of abnormal aggregation.

As has been pointed out by F. G. Donnan (*Phil. Mag.* 6, vol. i. 647), we have to account for the fact that a solid substance *C*, when brought in contact with certain liquid media, breaks up, or disintegrates into these media, but in such a manner that the disintegrating process does not proceed to the molecular limit.

The liquid medium seems to be interspersed with minute aggregates of *C*, which are still so much larger than their molecular magnitudes, that they are subjected to almost statistically uniform bombardment. These complexes are such that changes of temperature, or the addition of comparatively small quantities of other substances frequently cause the sudden precipitation in mass of the substance *C*.

This view of the case may be regarded, if we may use the term, as a very mechanical one. No provision is made for the possible arrangement of the system into aggregates which are made up of molecules of both solvent and solute such as we undoubtedly get in mixtures of alcohol and water, and in many other cases.

The first investigator to study the solution state of the " direct " or cotton dyes was Picton (*J.C. Soc.* 1892, 148). He made use of certain tests to establish the state of different solutions, and with them tested an aqueous solution of Congo red.

Tyndall had noticed that light is polarised by its passage through colloidal solutions. Congo red, which dissolves easily in water, was found under these conditions to give a well-marked polarised beam.

Filtered under pressure for two hours through a porous cell, the same solution passed through practically colourless. A slow diffusion experiment gave a similar result.

The molecular aggregation in aqueous solution of these dyes is also given by Krafft (*Ber.* 1899, 1608) as follows:

Benzopurpurin	3000	724	(normal calculation)
Diamine Blue	3430	999	,,

The following figures are given for

Rosaniline hydrochloride (mol. wt. 337)

In alcohol	330, 325, 343
In water	520, 589, 617

Methyl Violet (mol. wt. 407)

In alcohol	403.5, 421.1
In water	804.5, 838.7, 870.4

Methylene Blue (mol. wt. 319.8)

In alcohol	321.4, 342.7
In water	321.2, 492.4, 530.5

Tannic Acid (mol. wt. 322)

In water	1587

Picton (*ibid.*) further pointed out that the degree of aggregation in the case of Congo red varied with its state. An alkaline solution of this dye filtered readily, but the dye would not pass through the porous material in either the acid, or neutral state. The " equalising " action of alkali when dyeing with these colours may be explained on these lines.

It was also shown that Magdala red was not present in such a state of aggregation in aqueous solution, but would pass through the filter in neutral or acid solutions.

With a solution of silicic acid the aggregates were smaller than in the case of Congo Red, for they neither polarised light, nor failed to pass through the filter.

There are indications that the state of aggregation may be greatly in excess of that indicated by Krafft with the direct dyes.

It is interesting to note that there is certain evidence to be gained from some experiments on the effect of low temperature on dyes, that their solution state is different to the solid one. It has been shown that the effect of low temperature on the colour of dyes in the solid state or when dyed on fibres is nil. On the other hand, when in alcoholic solution some of them alter altogether, while others do not. This is a subject which is worthy of further study, both from the point of dyeing and from that of solution.

In the same way it is well known that the optical properties of substances are modified by the nature of the solvent. For instance, lævo-rotatory oil of turpentine (37.01° specific rotation) in 10 per cent. solutions gave the following results (Walker):

Solvent.	Specific rotation.
Alcohol	38.49°
Benzene	39.45°
Acetic acid	40.22°

It is clearly difficult exactly to define the nature of a solution of a colloid, but information on this point is being rapidly extended.

It has been stated by Henri and Mayer (*Compt. Rend.* 57, 34) that, when solutions of aniline colours are examined ultra-microscopically, they exhibit true colloidal properties.

Some work by these same investigators on the action of the β-rays of radium on solution of colloids is of interest. The solutions were exposed to the action of these rays for five days. Magdala red, methyl violet, and ferric hydroxide (positive) were decomposed.

On the other hand, solutions of aniline blue and some other negative solutions were unaltered. The action is said to be due to the negative charges of the β-rays discharging the positively charged colloids.

The stability of solutions of colloids may, in a way, be estimated by their resistance to centrifugal action. For instance, Franklin and Freudenberger have shown that colloidal solutions of platinum black and Prussian blue were completely separated at a high speed from the solution. The cause of this was attributed to supersaturation effects due to high acceleration of gravity (*Elect. Rev.*, vol. 47, 508). Such results indicate, within certain limits, the relations which exist between the solvent and solute in these special cases. The conception that the precipitation is due to supersaturation effects is also interesting, when it is remembered that the same idea has been put forward to explain the action of dyeing, the results in the latter case being attributed to surface concentration effects.

Otto Weber (*Chemistry of India Rubber*, page 69) contends that the term colloid should only be applied to compounds, the solutions of which under all conditions and in whatever solvents, behave as colloids, and which in their solutions fully maintain this character through all chemical changes.

As an absolute definition this may be satisfactory, but from a practical point of view it is not so unless we classify the substances as follows:

(1) Colloids (as Otto Weber's definition).

(2) Pseudo-colloids (substances which enter into pseudo-solutions in some solvents and solutions in others).

(3) Crystalloids (substances which behave with water as perfect solutions).

It will be seen that on similar lines no substance should be called a crystalloid unless it is perfectly soluble in all solvents, and in these solutions fully maintains this character through all chemical changes.

Such definitions, with our present knowledge, are perhaps out of place. The chief thing the dyer has to realise is the possibility of the solution state varying in the dye and mordant baths, the results which may be expected to follow from these changes, and their influence on the rate of absorption by the fibres introduced into these baths in the ordinary course of dyeing. Also that the state of solution may be varied by corresponding variations in the physical state of the dye liquor brought about by altered temperature, concentration, or by the addition of third substances (assistants, &c.) to the bath.

It is not advisable, perhaps, in a book devoted to the subject of dyeing from a more or less practical point of view, to dwell too closely on the theory of the constitution of colloids like cellulose, and their solution state. This work is of great interest from a purely theoretical point of view, and may ultimately influence the practical side of the question. It is too far-reaching, and perhaps at the present time too indefinite, to be considered here. That such ideas should ever have been put forward is, however, a sign that the future theories which will be brought forward to explain general reactions, may not be of a simple nature, but will emphasise the extremely complex nature of the reactions which make up some of our seemingly simple, and everyday operations in the dyehouse.

CHAPTER VII

PHYSICAL ACTION AND SOLID SOLUTION

THE study of dyeing from the physical point of view has served a purpose. The discussion of the subject has been widened, and much experimental work undertaken as a natural consequence.

In early days, as mentioned in chap. i., such investigators as Hellot and Le Pileur d'Apligny, with the support of Macquer, Berthollet, Bergman and Chevreul, favoured a purely mechanical basis for the actions involved.

Hellot in the year 1734 attributed to the pores of the wool fibre the power of opening and closing, and assumed that the dye particles lodged in these interstices. The astringent substances, which took part in the dyeing operations, were supposed to form a coating over the colour particles so fixed. A colour not protected in this way was assumed to be fugitive.

The "invisible mechanics of dyeing" was due to the opening of the pores in the fibre, the deposition of the dye particles therein, and the subesquent action of a material or cement, which held the particles in their place. He likened the general action to the very mechanical process of fixing a diamond in the bezel of a ring. The hot water opened the pores, the tiny atoms of dye entered, and the, tartar and subsequent cooling completed the operation.

He also suggested that if only the correct astringent could be found for the fugitive colours, they, too, would be fast. As it was they remained on the surface of the fibre, or were imperfectly fixed in its substance.

Le Pileur d'Apligny subsequently lent his support to this theory, and extended it to other fibres, such as silk, cotton, flax, &c., holding that the mechanical state of the different fibres accounted for the variation in their dyeing properties. Wool, said he, was composed of a number of individual hairs containing a marrow, or fatty substance. These fibres, in fact, were pipes perforated through their whole length, and laterally, with an infinitude of orifices. By these the foreign substances were admitted to the central cavity, after the removal of this marrow. In this way he claimed that wool was the most porous of all fibres, and is, therefore, the most easily dyed, and at the same time absorbs a relatively large proportion of dye substance.

Silk he considered to be only dried animal jelly, which in its natural drying only produces pores and inequalities on its surface. These only admit colours in a dilute form, and with great difficulty. Thus, said he, silk is the most difficult fibre to dye, and cotton stands half way between wool and silk. In trying to follow his arguments it is necessary to remember the conditions under which he worked, and the dyes at his command.

In this way it was assumed that dyeing was purely a mechanical process. Wool might be dyed a scarlet colour, cotton remain colourless, and silk only take a dirty hue. He contended that the cochineal tin lake particles were too large to enter the cotton, or silk fibres, but that they would readily enter the wool pores. Silk admitted the impurities because they were simple (soluble ?).

He further pointed out that this varying action might come into play even in the same fibre.

For instance, the condition of the fibre as regards weaving and spinning might influence the result. In this way he explained the incomplete dyeing in the interior of wool dyed with this scarlet lake, as compared with goods alumed before dyeing. This ultra-mechanical theory passed from the hands of these two early experimenters in a highly developed state, and little seems to have been done in adding to, or elaborating it until one hundred years later.

At this point, and under the altered conditions of dyeing, the additional knowledge of the fibres, and general science, Walter Crum published some further work on this subject (*J.C.S.* 16. 1. 404). This investigator seems to have been profoundly impressed by the work of De Saussure, on the absorption of different substances and gases by charcoal, and he came to the conclusion that several of the operations in dyeing were due to the capillary action described by this chemist, thus introducing a new refinement into the theory at the end of this long interval of time. He also based his application of this theory to the dyeing of fibres, on the physiological work of Thompson and Bauer. Their work introduced the microscope in the study of fibres, and thus established a fresh method of examination. As the result of their investigation they set forth the idea that the vegetable fibres were glass-like tubes. After the ripening of the fibre, the central orifice, owing to the flattening of the fibre, presented the aspect of two separate tubes.

This next step in the mechanical theory was the result of four experimenters' work, and to the research student in dyeing this affords a simple yet satisfactory example of the possible influence of one worker's results on those of others.

Crum held that mordants are decomposed in the interior of these tubes, having entered by the lateral openings; the oxide being set free in these narrow passages is effectually held in position. When, therefore, the washed cotton passed into the madder bath, the mordant and dye combined chemically to form the dye lake. This investigator explained the fixings of the oxide to the fibre in the following way. A natural decomposition of the mordant solution took place " just as it would be decomposed in similar circumstances without the intervention of the cotton." He speaks also of sacs in the fibre substance lined by metallic oxides. The arguments he based these theoretical conclusions on may be summed up as follows :

(1) If it is assumed that the mordant enters into chemical combination with the fibre, it must lead to its disintegration. He removed the mordant from the fibre by chemical means, and found that this was not the case.

(2) Under the microscope the colour is distributed on the internal sides of the tubes.

(3) The dyeing of indigo blue supports the idea that there is no chemical combination in the proper sense of the word between the fibre and the dye, when the nature of the reaction is considered.

Whatever may be the ultimate place assigned to these theoretical considerations, this investigator introduced a new method, of examination, viz., comparison of the physical properties of the fibres by the aid of the microscope before and after dyeing.

Again we have a long interval before these ideas were directly attacked, and disproved in some details. De Mosenthal has recently shown (*J.S.C.I.* 23, 292) Crum's idea—that the cotton fibre is dyed by capillary action—to be incorrect. Single cotton fibres exhibit no capillary action. Several fibres must be in contact for the liquid to rise. Crum's idea that the cuticle is non-porous is also incorrect. It is very porous. These experiments are calculated to modify our ideas on the action of dyes on the cotton fibre, and to throw us back to the ideas advocated in the eighteenth century as to the physical nature of the cotton fibre.

We now consider in detail the many arguments and experiments brought forward in favour of a simple mechanical theory.

It was pointed out many years ago that neutral filters, such as sand in layers, will remove colouring-matters and salts from solutions. Here we have large surfaces of such an inert substance as fused silica retaining, in some way, or other, notable quantities of salts, coloured or otherwise. This filtering action must undoubtedly be intimately connected with surface action.

We pass on to the careful work of Mills and Hamilton (*J.S.C.I.* 1889, 263), dealing with the action of mixed colours on wool and their relative absorption by the fibre.

The colours chosen were Victoria Blue 4 R and berberine hydrochloride. The conditions of experimenting were exact. The temperature chosen might have been higher than 40° C. The authors indicate that different results might have been obtained at 95°. The result arrived at is expressed in the following rule: "The proportion of blue to yellow deposited in the fibre is the same as that in which they existed in the vat before dyeing."

That is to say, the shade of the mixture in the dye-bath remained the same as that which existed in the vat before dyeing. The shade of the dye-bath was tested by the detached colorimeter (*Phil. Mag.* 1879, 437).

With varying quantities of the colours it was found that the total quantity of colouring-matter deposited on the fibre is least when the weights of the blue and yellow are equal, and that it becomes greater as the disparity between the weights increases. The simple mathematical treatment of finding an equation for each of the dyes separately was adopted. The equation was of the following order:

$$y = a + \frac{\beta x}{1 - \mathrm{T}x}$$

y being the reciprocal (= 5) of the total constant quantity (.2) of dye-stuff taken as a reagent, and β and a constants of attraction and other conditions. The constant a represents an attraction not directly due to the dyeing process as such, x is the weight of the colour taken, y the weight of the colour deposited on the fibre.

The conclusions arrived at from these equations are that in the case of dyeing wool with mixed solutions of these dye-stuffs, there is deposited at first a certain small amount of dye-stuff (x) irrespective of the amount of each dye-stuff taken, and then the dye-stuff taken up is proportional to its own mass, and inversely proportional to the mass of the other colours.

The mechanical theory also receives the support of L. Hwass (*Farb. Zeit.* 1890-1, 224); von Prager (*ibid.* 356), and Spon (*J.S.C.I.* 1893, 559).

The assumption is made that the dye-stuff is the same in the fibre as in the free state, for it may be diazotised and combined with phenols and amines to form azo dye-stuffs. The writer of this book pointed out that this is not so in all cases, or at any rate, the "developing" of some colours on silk is exceedingly slow; therefore, when Möhlau (*Zeit. Ang. Chem.* 1893, 225) shows that sand will "dye" with naphthol azo colours which are insoluble in water, the case for a mechanical theory is on this point made out. The dye is said by this investigator to enter the pores of the silica. The dyeing method is as follows:

(1) Dyeing with β-naphthol dissolved in NaHO.

(2) Diazobenzene chloride added to this solution after sand has been worked in it.

Asbestos, in the same way as sand, will dye in solutions of some colours (*Spon, Dingl. Polyt. J.* 1893, 287).

It has been noticed by Pokorng (*Bull. Soc. Ind. Mulh.* 1893, 282), that wool and silk are able to attract from aqueous suspension certain insoluble amines. All that is necessary is that they shall be present in a state of fine division. Naphthylamine dissolved in a small quantity of alcohol and poured into water will impregnate wool if left overnight. This matter will be further discussed elsewhere.

The fact that many colours "rub off" is held to be in favour of the mechanical theory, it being assumed that this is an indication that the colours are not in chemical combination with the fibre.

The influence of temperature on dyeing action is a very important factor, and may indicate the nature of the reactions which take place in the dye-bath. Chemical action, generally speaking, was calculated by Hood (*Phil. Mag. May.* 1878), from data obtained from Harcourt and Esson, to be proportional to the square of the temperature.

The results obtained by Mills and Rennie (*J.S.C.I.* 3, 215,) by experimenting with wool, and dyeing with rosaniline acetate, will be remembered (*see* page 99).

The results then obtained may be tabulated as follows:

Temperature of dyeing.		Result.
—1.16°C.	..	No colour deposited
31.11°C.	..	Maximum colour deposited
81.15°C.	..	Very little deposited
100.0°C.	..	Fair amount deposited

Hood's law is not obeyed here. The reversal of action above the comparatively low temperature of 31° C. may be due to the increasing solubility of the dye in aqueous solution.

The reverse action above 80° C. may be due to the fact that basic dyes undergo some change above this temperature.

It is stated that somewhere about the boiling temperature rosaniline salts are dissociated. In weak solutions the colour is entirely destroyed if adequate time be allowed for this action (*J.C.S.* 35, 38). In practical dyeing with these colours very slight excess of colour should be used, and the temperature kept about 40°–50°.

The action of direct dyes on cotton, which has been a difficulty in the way of a chemical theory, has been studied in more or less detail by Gnehm and Kauffler (*Zeit. Ang. Chem.* 1902, 15, 345).

The barium salt of benzopurpurin dyes without decomposition, and a similar result is obtained with the sodium salt. The free acid seems to dye equally well when a time allowance is made for the decreased solubility of the same in water. Similar results were obtained in the case of benzoazurin, which contains no amido groups, and, therefore, cannot form a salt with cellulose.

A hank of cotton dyed with benzopurpurin (sodium salt) will on prolonged boiling with a similar but undyed skein, give up its dye until an equilibrium of colour is obtained on both skeins.

The action of acids on Congo Red dyed on cotton is said to indicate that the dye is present in the free state, and not combined with the fibre. Weber stated that the cellular cotton absorbed the hot solution of the dye, and that on cooling the skein the dye was precipitated. This is, of course, the idea of some of the early investigators. If this method of argument is correct, the action of acid proves equally well that the dye is free in the case of silk dyeing, for the same effect is noticed there with this dye. It is interesting to note that the natural moisture in the cotton fibre is said to be essential to colour-production. If this is removed (by alcohol) the colours are dirty and dull. It will be remembered that drying does not seem to produce this effect. The idea that the benzidine or direct colours dye because their rate of diffusion is less, is supported by the same authority. Croceine 3 B will not dye cotton, but its barium salt will do so. Fairly dark shades are produced even after washing. The rate of diffusion is said to be greatly retarded in this case.

In 1894 (*J.S.C.I.* 13. 95) I assumed a mechanico-chemical theory of dyeing to be the correct one, a theory which depended primarily on a diffusion process obeying a modified form of the general laws of osmosis as then stated, supplemented by a chemical reaction or series of chemical reactions between the fibre and the dye, Fick's law being held to govern the introduction of the colour to the fibre. Zacharias (*Farb. Zeit.* 1901, 1149) also brings this to notice, and seems to favour it.

As I then pointed out, Fick's law had been verified for gelatine and agar-agar solutions. In the case of animal membranes a retarding action was noticed and the results obtained here were roughly one half those obtained by the purely osmotic pressure. The flow of the dissolved substance was hindered, but not stopped, by the organised nature of the membrane.

The possible influence of dissociation on the action of dyes in solution must be considered. Briefly, the condition of electrolysis in solution has been stated as follows.

Neutral salts, as a general rule, are strongly dissociated in aqueous solutions. In dilute solutions it is held that they are entirely dissociated.

The salts of the alkalies are very readily dissociated. The acids vary in their degree of dissociation. Their acid properties seem to be due to the hydrogen ions. The strongest acids are those which are most completely dissociated.

Water itself is dissociated to a small extent, so that it can act as an extremely weak acid or base, as the case may be. Thus, Walker has shown that when hydrochloric acid is added to a solution containing urea, the acid divided itself between the water and the base.

Dissociation of dyes may possibly take place in dye solutions of the ordinary strength.

Magenta is dissociated in water and alcohol. The experiments of Fischer and Schmidner with strips of blotting-paper are well known. They show the dissociation of double salts, the salts rising according to their relative rates of diffusion. It has been shown (v. Georgievics) that with magenta, twenty times the amount of chlorine necessary for the magenta base diffused in this way. The examination of the electrical conductivity of magenta solutions leads to the same conclusions (Miolati, *Ber.* 26, 1788), viz., that dissociation takes place in aqueous solutions.

It has been pointed out by Silbermann (*Chem. Zeit.* 19, 1683), that in any specific series of dyestuffs, increase in molecular weight is accompanied by decreased solubility, and it is stated that the rate of absorption of the dye is correspondingly decreased. Assuming that high molecular weight means high molecular volume, the dyes will take longer to diffuse between the intermolecular spaces of the fibre and longer to leave it also.

This does not seem to be the case with the primuline colours (Dreaper, *J.S.C.I.* 1894, 95). It may be, however, that the fact that the heavier dyes take longer to diffuse, indicates that in practice they are fixed in greater proportions on the external area of the fibres. This might confuse and obscure the real nature of the reaction, so far as pure absorption results are concerned.

Hallitt (*J.S.D. and C.* 15, 30) has made a number of interesting experiments with the object of explaining the action of sodium sulphate in the dyeing of wool. The ideas in vogue when he wrote his paper were expressed in the "Manual of Dyeing" as follows:

(1) That the raising of the temperature in dyeing by the addition of the sulphate increased the dyeing effect.

(2) The sulphate keeps the dye in a fine state of suspension.

(3) Bisulphate is formed with the H_2SO_4, and as a consequence the dye is not so rapidly transferred to the fibre.

The fact that 100 per cent. on the weight of wool of sulphate of soda will only raise the boiling-point .75° C. shows that the effect on temperature of the bath may be neglected in practice. It may be mentioned in passing that we have no knowledge of the effect of increased temperature on dyeing above 100° C. Hallitt does not consider that the sulphate acts by keeping the dye in a fine state of suspension. He points out that acid colours are more easily stripped off wool by sodium sulphate than by either water or sulphuric acid.

Yarn boiled for ten minutes in the following solutions after being dyed with Carmoisine B. lost the following amounts of dye.

Solution.	Colour extracted.
Water	.15 % of total present.
5 per cent. H_2SO_4	.18 ,,
50 ,, Na_2SO_4	4.40 ,,
50 ,, NaCl.	2.40 ,,

The percentage of substances added is on the weight of yarn, and the proportion of yarn to liquor is 1/50.

In some cases the stripping of the colour goes on beyond the point of saturation of the dye in the solution. This remarkable result is seen when dark shades of indigo extract on wool are treated in this way. The dye may be partly thrown out of solution as a precipitate.

It is noticed, too, that an amount of sodium sulphate in excess of that required to form the bisulphate still acts, and will influence the dyeing.

Uneven skeins, where the dye is in patches, will equalise, if boiled with a solution of sodium sulphate. This equalising action is seen when Palatine Red A is dyed with

(*a*) 6.8 per cent. HCl.
(*b*) 6.8 per cent. HCl. + 20 per cent. Na_2SO_4 (cryst.)

The first solution gives a very uneven result, and the second an even one on wool fibre.

In considering these experiments with wool where the dyeing occupies some time at the boil, it is as well to remember that the wool has an absorbing action on the acid. Knecht found that if 5 per cent. of acid was present in the bath at the beginning of an experiment, only 1.5 per cent. remained in solution at the end of the dyeing (*J.S.D. and C.* 1888, 105). These experiments are said to indicate that the action of dyeing is equivalent to chemical action in dilute solutions.

From this point of view, the point of equilibrium between the amount of dye in the solution and on the fibre is a movable one. The addition of acid increases the amounts fixed on the fibre, while the addition of sodium sulphate has the opposite effect. The effect produced by either of these additions varies with different colours.

When hydrochloric acid and sodium sulphate are in solution together, we can express the reaction between them as follows:

$$2HCl + Na_2SO_4 \rightleftarrows H_2SO_4 + 2NaCl.$$

By Guldberg and Waage's law of chemical action we know that the velocity of change at any moment varies directly as the product of the number of equivalents of the factors of change present in unit volume of the medium of change.

The result arrived at is, that the even dyeing of any acid is proportional to its acidic intensity.

An exception has to be made in the case of sulphuric acid, which gives abnormal results. The intensity values of acids are as follows:

Nitric acid	1.00
Hydrochloric acid	1.00
Sulphuric acid	.49
Oxalic acid	.24
Citric acid	05
Acetic acid	.03

Taking values from this table, and with quantities of acids representing equal intensities, we obtain the following results, one per cent. of Palatine Red being used in each case.

Acid in dye bath.			Colour left in bath.
6.84	per cent.	hydrochloric acid	.13 per cent.
15.62	,,	oxalic acid	.15 ,,
6.12	,,	sulphuric acid	.90 ,,
477·6	,,	acetic acid	.15 ,,

Here we have a fairly close agreement, if we except the case of sulphuric acid.

A possible reason for this action is that the wool removes an abnormal amount of sulphuric acid from the solution. The following results seem to show this is the case.

Per cent. of acid present.	Proportion of free acid left in solution.	Proportion of colour left in solution.
11.4 HCl.	36.4	.08
5.0 HSO_4	26.6	.90
6.1 oxalic acid	35·5	.30
23.8 acetic acid	60.0	5·25

A much smaller proportion of sulphuric acid is left in the solution. This action, therefore, may be due to greatly decreased mass action. The chief action of acids has been said to be on the wool fibre itself. Knecht has shown that wool treated with acid and washed to neutrality, dyes well in a neutral solution of colour acid.

This matter is not, however, clear. If the sulphuric acid is taken up in abnormal quantities, it would follow that the fibre is more acted on in this case, and, therefore, other things being equal, the dyeing should be more complete.

It is clear, at any rate, that the direct action of the acid is modified in some way by the presence of sodium sulphate or sodium chloride. Sodium sulphate is one of the products of the direct change which takes place between colour acid and salt, and by largely increasing its mass in the solution by direct addition, the point of equilibrium is pushed back, and more free acid remains in solution.

Therefore, by the addition of sulphate the dye is stripped from the fibre. The facts seem to be in accordance with the laws of equilibrium.

The colour acids of Scarlet 2R and Orange G will dye wool very feebly. In fact, they are said hardly to stain the fibre at all, and in the former case not so deeply as its sodium salt.

An addition of 3 per cent. sulphuric acid will drive on a large proportion of these dyes, and 3 per cent. hydrochloric acid will exhaust the bath.

With Cardinal red the colour acid gives a better result. In this case about half the dye goes on to the fibre without the addition of any acid.

This research, which is clearly of interest to the wool dyer, is also of equal interest in other ways. It is an example of the work that might be done in our dyeing colleges if some definite scheme for technical research was adopted.

The effect of varying temperatures of the dye-bath may be mentioned here.

We have seen the extreme importance of temperature in mordanting, and how this varies with the fibre. Silk and cotton give the greatest effect in the cold (except when tannic acid is used as mordant).

The dehydrating effect of a high temperature in dyeing on some mordants may even prevent the formation of a lake, as has been pointed out in dyeing cotton with alizarine; and every dyer experienced in dyeing alizarine on alumed silk will have noticed the same effect.

The action of tannic acid on animal fibres and substances generally is an important one. There are dye-houses in the south of France, and elsewhere, entirely devoted to dyeing silk black with tannin extracts on mordants. Before the introduction of the direct dyes tannic acid was very largely used in mordanting cotton for basic colours.

Its action in the case of tanning leather is well known. The tannin is said to combine with the material, reducing its permeability by water and modifying it in other ways.

A similar action is noticed with silk. Gallic acid is not absorbed to the same extent as tannic acid, although a process proposed some time ago for the separation of these two acids by absorption by silk is of little value.

Gallic acid will not precipitate so soluble a proteid as gelatin, but in the presence of tannic acid both acids are carried down.

Tannic acid is absorbed by cotton, but gallic acid is not under ordinary circumstances. It is not known whether it is absorbed in the presence of tannic acid.

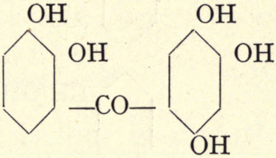
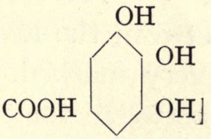
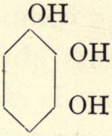
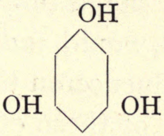
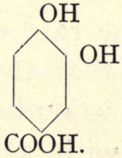
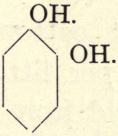
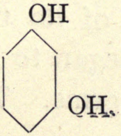
Tannic acid is absorbed by cellulose in its various forms as follows (Knecht, *J.S.D. and C.* 1892, 40):

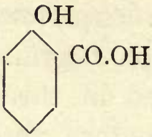
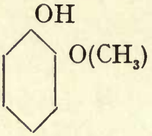
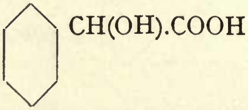
Form of cellulose.	Tannic acid taken.	Tannic acid absorbed.
Bleached cotton	.25 grms.	.0513 grms.
Unbleached cotton	do.	.0563 ,,
Mercerised cotton	do.	.1033 ,,
Pptd. cellulose	do.	.1525 ,,

Further work on this subject has been done by Gardner and Carter (*J.S.D. and C.* 1898, 143), and the relative action of tannic and gallic acids on cotton confirmed. The theory that absorption is mainly due to physical action is not considered by these investigators to be supported by the fact that the regenerated or precipitated cellulose has an increased affinity for tannic acid. On the other hand, the acid is easily removed by cold, or boiling water.

The action may be of a secondary nature, and the water replace the tannic acid by mass action.

A series of experiments with different aromatic phenols was made with the following results, the conditions of the experiments being as follows: Strength of solution 1 grm. per litre; 10 grms. of cotton were soaked in this for three hours. The percentage of substance absorbed is given in each case.

Reagent.		Percentage absorbed.
Gallotannic acid		32
Catechutannic acid	do.	32
Gallic acid		0
Pyrogallol		4·5
Phloroglucinol		24–26
Protocatechuic acid		0
Pyrocatechol		0
Resorcinol		45–50

Salicylic acid		0
Guaiacol		0
Mandelic acid		7–8

The difference between the absorption of tannic and gallic acids is very marked.

The difference between the 1.2.3 trihydroxybenzene and the 1.3.5 compound is also noticeable.

The different results obtained with the 1.2 and 1.3 dihydroxybenzenes is still more marked and, if it were not that the suggestion is negatived by the figures for pyrogallol, would indicate that the meta position has some influence on the absorption factor.

A general survey of these effects of the OH and COOH groups on the rate of absorption makes it difficult to imagine that the action is a chemical one. There is no question here of a phenol combining in some way with a diazonium compound. Kœchlin found that cotton saturated with tannic acid in a 50 grm. per litre solution was still able to absorb tannic acid from a 20 grm. solution. It retained the whole of its tannic acid in a 5 grm. solution, and only began to lose it when the strength was reduced to 2 grms. This action is discussed elsewhere. The action seems to be reversible in this case.

The effect of the addition of fatty acids to the tannic acid solution is as follows:

Solution.	Absorbed.
Tannic acid alone (as above)	32 per cent.
+ formic acid	48–50 ,,
+ acetic acid	48–50 ,,
+ propionic acid	48–50 ,,

The acids were present in quantities equivalent to 4.5 grm. acetic acid per litre. From a chemical point of view the increased absorption of one acid in the presence of another is an abnormal one.

With stronger acids this ratio does not hold, as the following figures will show.

Solution.	Absorbed.
Tannic acid alone	32 per cent.
+ acetic acid	48–50 ,,
+ citric acid	19–21 ,,
+ tartaric acid	20–22 ,,
+ sulphuric acid	18–20 ,,
+ hydrochloric acid	30–32 ,,
+ sodium acetate	16–18 ,,

The effect of varying the percentage of acetic acid on a solution of tannic acid (1 grm. to litre) is as follows:

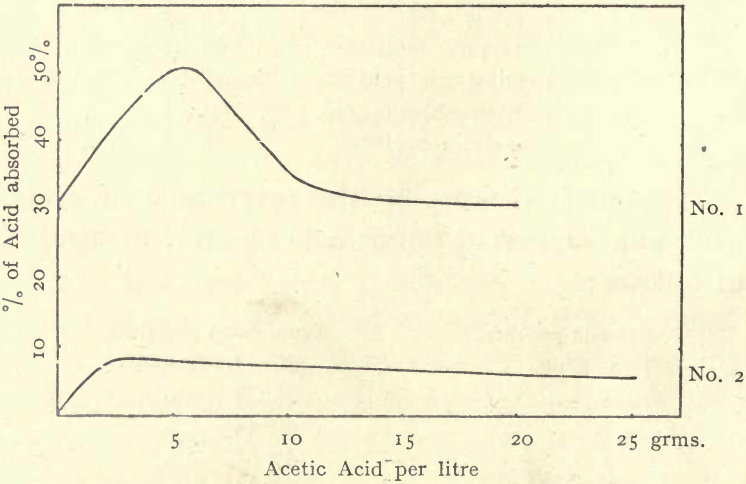
Acetic acid per litre.	Tannic acid absorbed.
0 grms.	30–32 per cent.
1 ,,	35–36 ,,
2 ,,	40–42 ,,
5 ,,	49–51 ,,
10 ,,	32–34 ,,
20 ,,	31–32 ,,

This rather negatives the idea that the action of the acetic acid is on the fibre rather than on the acid in solution.

An action of a similar order is noticed in the case of gallic acid (1 grm. per litre).

Acetic acid per litre.	Gallic acid absorbed.
.0 grms.	0 per cent.
·5 ,,	2 ,,
2.5 ,,	8.5 ,,
5 ,,	7·5 ,,
25 ,,	5·5 ,,

These results should be extended to the animal fibres, and to precipitated cellulose (artificial silk). They are of great interest from a theoretical as well as from a practical point of view. The influence of the addition of acetic acid to the solutions is clearly shown in the following curves, the figures being taken from the above results.



ABSORPTION OF TANNIC AND GALLIC ACIDS IN PRESENCE OF ACETIC ACID

These curves show clearly the influence of the addition of acetic acid on the absorption of tannic and gallic acids by cotton. The concentration of the aromatic acid was in each case 1 grm. per litre, and the acetic acid was added up to a strength of 25 grms. per litre.

The reversal in the action is clearly seen in both cases, and occurs at a comparatively early stage.

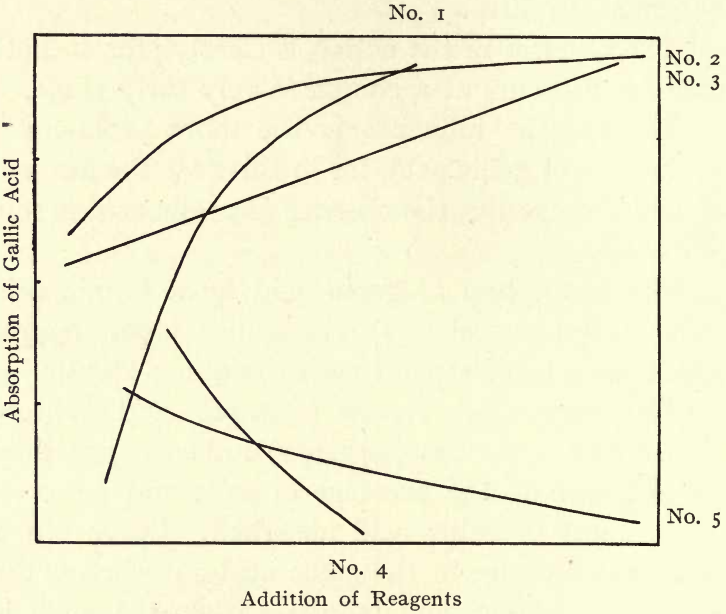
Perhaps the influence is the more pronounced in the case of gallic acid, for in this case the amount of acid absorbed in the absence of acetic acid is said to be nil.

The absorption of gallic acid by a tannic acid collin (soluble gelatine) coagulum gives figures which do not correspond with the above results.

The curves on p. 164 (Dreaper and Wilson, *Proc. Chem. Soc.* 1906, 22, 70) indicate generally the influence of the presence of salts and acids on the amount of gallic acid absorbed. Curve No. 1 shows the increase in the gallic acid absorbed as the amount of tannic acid increases when the collin is added to the mixed acids. When the gallic acid is added after precipitation the result is practically the same. Nos. 2 and 3 indicate the increased absorption in the presence of sodium and ammonium chlorides, Nos. 4 and 5 the decreased absorption in the presence of hydrochloric and acetic acids respectively.

Gelatin in the hydrogel state absorbs gallic acid, although no coagulation takes place when these two substances in solution are mixed together. Salts increase this absorption and alcohol reduces it.

Albumin absorbs gallic acid when precipitated by tannic acid or heat. Alcohol prevents this action and also the absorption of tannic acid. In very concentrated solutions gallic acid precipitates albumin.



ABSORPTION OF GALLIC ACID BY COLLOIDS

Similar results were obtained when silk or hide powder took the place of albumin, and there seems to be a great similarity in the reactions with these different organic colloids—the curves, so far as they go, indicating that the taking up of tannic and gallic acids by organic colloids is chiefly a matter of absorption.

The writer has pointed out that as osmosis probably plays an important part in the process of dyeing, it might be possible to institute experiments comparing the relative osmotic pressure of dyes through inert membranes on the one hand and fibres on the other.

Whatever the ultimate process of dyeing may be, it seems necessary to assume that the dye enters the fibre substance by direct diffusion.

As I then pointed out, the general laws of diffusion would probably govern this method of introduction, although it must be remembered that these will only apply to substances in a more or less perfect state of solution. The laws are as follows :

(1) The pressure (osmotic) is proportional to the concentration of the solution, or proportional to the volume in which a definite mass of the substance is contained. This law only holds good for inert substances.

(2) The pressure increases for constant volume proportionately to the absolute temperature.

(3) Quantities of substances (dissolved) which are in the ratio of the molecular weights of the substances exert equal pressure at equal temperatures.

It should not be impossible to find whether the dyeing action is in conformity with these laws, or is complicated by further reactions as indicated elsewhere.

The present state of our knowledge does not supply figures which are available for this investigation. As mentioned elsewhere, it is known that animal fibres materially modify this process. The results obtained are, roughly, half those obtained by the true osmotic pressure, when exhibited in the case of solutions of agar-agar or gelatine.

It would seem from the above recorded experiments with tannic and gallic acids, that the absorption of the latter acid was as perfect when the coagulum of tannic acid and collin was first formed as when the gallic acid was actually present at the time of formation. The rate of diffusion in the former case is therefore very rapid and complete.

Fick's law "that the quantity of salt which diffuses through a given area is proportional to the difference between the concentration of the two areas infinitely near to each other," was found not to be true for animal membranes. An osmotic pressure exists, but it does not reach its true value (*Zeit. f. Phys. Chem.*, 3, 316).

It is clear that the fibre substance must be permeable in order that dyeing may take place; this is indicated by the fact that nitrocellulose in the fibre state will dye readily, but when in the state of a film (prepared by dissolving in acetone) it will not do so, or at any rate the action is a very slow one.

The dyeing of wool may be prevented by treatment with sulphuric acid, hypochlorite of soda, and stannous chloride (*Fr. Pat.*, 318741). So that here we have a mineral acid, an oxidising agent, and an acid reducing reagent acting in the same direction, so far as colour absorption is concerned.

The action of solvents for dyes on dyed fabrics also gives interesting results.

This action is noticed in other parts of this book. Most colouring-matters, acid, basic, or direct, and even the mordant and developed colours are all said to be soluble in either 90 per cent. acetic acid, or absolute alcohol, if not in the cold, at any rate when heated.

It is an interesting fact that some of the acid colours on wool will not yield to alcohol, but will readily leave the fibre if a small quantity of water is added (Pokorng, *Bull. Soc. Ind. de Muhl.* 1902, 245). This may be due to the fact that absolute alcohol cannot penetrate the wool substance. When a small quantity of water is present the fibre substance becomes sufficiently hydrated for the spirit to enter.

Patent Blue and New Crocein are examples which will illustrate this action.

The successive action of 90 per cent. acetic acid and spirit will remove almost any colour.

In the case of cotton it would seem that the structure of the fibre will allow of the action of other liquids than water.

It is recorded, for instance, that alizarine lakes dissolved in alcohol-ether will dye cotton. It is not known, however, if silk and wool will dye in this solution.

Amyl alcohol will apparently act in the same way. Rosaniline dyed on silk from an aqueous solution is partly soluble in this solvent, and an equilibrium is said to be established between the dye in solution, and the dye on the fibre (Sisley, *Bull. Soc. Chem.* 1900).

Solid Solution.—The phenomenon of solid solution was first noticed by van't Hoff in 1890 (*Zeit. f. Phys. Chem.* 5, 322). This idea of the solution of one solid in another was brought forward to explain certain facts recorded in connection with alloys, and salts of similar molecular constitution, or structure.

The suggestion that solid solution might be a universal phenomenon was not put forward, but that sodium sulphate and potassium sulphate, or silver and lead respectively, were capable of dissolving one another under certain conditions.

Witt, in 1890 and 1891, advanced the hypothesis that dyeing might be a case of solid solution.

If this were so, the range of solid solution must be widened to include the solution of various inorganic and organic substances in the fibres. The idea presented here is that the dye-stuffs are not only held by the fibre substance, but actually enter into solution in it.

The dye in the fibre was considered to be in the same state as the oxides which are soluble in precious stones (*Farb. Zeit.* 2, 1-6). Witt considered that the fact that fibres are red, and not bronze green, when dyed with magenta, and blue, and not bronze green when dyed with aniline blue, supported this idea. Rhodamines, also, will only fluoresce in solutions, and they do so on fibres. That magenta is taken up by silk would be explained by its being more soluble in it than in water. If a solution (alcohol) in which the dye is more soluble be taken, the fibre will not dye to the same extent.

The effect of trying to dye cotton with magenta may be likened to the action of benzene on a solution of resorcinol in water. The relative solubility of the latter is so much in favour of the water that the benzene cannot absorb it. On the other hand, ether is able to do so, and removes the resorcinol. In this way the action of the ether is compared to that of silk. The benzene may, in the same way, be compared to the cotton fibre.

Again, amyl alcohol may be compared with a phase where the dye is imperfectly removed from the dye-bath, for it only partly removes the resorcinol from aqueous solution.

The weak point in this argument is the indiscriminate way in which ordinary solution and solid solution are assumed to be similar in nature so far as their actions are concerned, and the universal nature of the interchange. This is not in accordance with the recognised theory of solid solution, nor have any facts been brought forward which would allow of such an arbitrary extension of this theory to cover the reactions which take place in dyeing.

It is considered also that the different shades given by the same dye to different fibres may be explained by solution. Isonitrolic acid, which is colourless, dissolves in benzene with a blue colour. Why should not the changes in dyeing be due to a similar condition ? The action of dyeing in the case of adjective colours is said to be similar to the action of benzene to which benzoyl chloride has been added. The resorcinol in this case is taken up by the water.

It may be gathered from this statement that Witt even suggests that the adjective colours are soluble in the mordants. If this is so, we must assume that no definite chemical combination takes place between the mordant and dye, and that the definite lakes isolated by Liechti do not exist.

The weak points in the above argument have been pointed out by v. Georgievics (*J.S.C.I.*, xiv. 149).

Magenta finely powdered and mixed with chalk gives a red, and not a bronze colour. If the crystals are rubbed between glass plates, the same result is noticed. The colour of the crystals is, therefore, shown not to be the natural colour, but an abnormal one, due to the dispersion of the light on the surface of the crystals or thick layers. If wool be dyed with a very concentrated solution of magenta it bronzes.

Fluorescence is held to be possible in the solid state. Fluorspar and barium platinocyanide are notable examples of this. Silk dyed with rhodamine is fluorescent, wool is not. Is the first an example of solid solution, and the second not? Fluorescence in fibres, it is contended, is due to a surface action.

If the dyeing of wool is due to selective solution it should be correspondingly reversible. This is not the case with many dyes. Also, if wool takes up more colour at 100° C, the dye should be more soluble at that temperature, and consequently might be expected to give up its dye again to water at a lower temperature.

The fact that the structure of the fibre also plays some part in the reaction is also against this theory.

On a later occasion (*Monatsh. für Chem.* 25, 705) v. Georgievics gives the results of experiments with indigo carmine, varying the ratio of fibre to solution, concentration, and amount of sulphuric acid present, singly, and in pairs.

The following law was found to express the results obtained:

$$\frac{\sqrt{CW}}{CS} = K.$$

CW = dye-stuff in 100 cc. after the process of dyeing.
CS = dye-stuff in 100 grms. silk after the process of dyeing.

This would agree with the requirements of van't Hoff and Nernst's modification of Henry's law of solution, and it would follow that the dye-stuff exists in silk in a simpler molecular condition than in water. With concentrated solutions the value $\frac{\sqrt{CW}}{CS}$ increases. This would point to the presence of more complex molecules in solution. In spite of these results the non-reversibility of the process is against a theory of solid solution. The writer of this book has given figures showing the extra fastness of dyes dyed ingrain over the same colours dyed direct, in terms of their resistance to the action of boiling soap solution. This result seems to be a general one, and extends over the dyeing of silk, wool and cotton.

These results are very difficult to explain by the solid solution theory. No explanation can be given which will explain this difference in "solubility."

It has been claimed that the abnormal action of jute fibre (lignocellulose) on ferric ferricyanide solution supports the solid solution theory (Cross and Bevan, *J.S.C.I.* 12, 104). If such a solution be prepared by mixing equal parts of N/20 ferric chloride and potassium ferricyanide solutions, and the fibre be soaked in this colourless solution, it is dyed a dark blue shade, and gains 20-50 per cent. in weight. Under the microscope the fibre appears an intense transparent blue, exhibiting, it is claimed, all the characteristics of solid solution.

This is possibly not a correct assumption; the ferric ferricyanide may be present in the colloid state. Jute fibre will not absorb the oxide from ferric chloride solution alone (only 0·4 per cent.). The small amount fixed is partially reduced. The absorption of oxide from a ferric chloride solution by a fibre would be an extraordinary one. The authors are perhaps straining a point in arguing from the ferric chloride solution to the ferric ferricyanide one.

They claim that the action in the case of the ferric ferricyanide is a specific one, and contend that the necessary reduction to the ferrous state takes place in the fibre, and not in the solution. It is argued that the fibre precipitates the ferricyanide, and that this is followed by a rearrangement of its constituents and production of the blue compound.

A solution of gelatine was found to precipitate this ferric salt in an almost quantitative way. This may confirm the writer's opinion that the ferric ferricyanide is present in the colloid form, and not in a state of solution as supposed by Cross and Bevan.

As the jute fibre contains an aldehyde group, and a lignone, or quinone containing a CO group and OH groups with phenolic functions (*Chem. Soc. J.* 55, 199), it is contended that this will account for:

(1) The deoxidation of Fe'''; (2) union of ferric and ferrous oxides; (3) combination with HCN.

The authors do not consider that dyeing can be of such a simple nature as Vignon assumes, viz., the interaction of groups of opposite nature (acid and basic).

So far as the colour is concerned, they assume that in the complicated cyanide we have to do with a C_6 ring and a quinoid constitution. This falls in with Armstrong's theory of colour (*Proc. Chem. Soc.* 1888, 27; 1892, 101).

Returning to this subject when criticising two papers attacking the solid solution theory (Weber, *J.S.C.I.* 13, 120; and Dreaper 13, 96), Cross and Bevan (*J.S.C.I.* 13, 354) deny that the reduction and fixing is caused by contact action with the aldehyde groups of the fibre, and they distinguish between the process, which may be chemical, and the product, which is a solid solution. The authors consider that in the dyed fibre the state of the dye is one of dissociation or molecular simplification, similar to that known to prevail in gases. At any rate, in dilute solutions they regard the action of dye and fibre as a case of ordinary solid solution. Magenta can be dissociated in solution by prolonged heating, but with a complete loss of colour. They also consider that the extreme sensitiveness of diazotised primuline produced in the fibre is a result of solution.

In a fully developed ingrain dye they consider that we have a chemical bond of union between the dye and fibre. The fact, however, that this diazotised primuline "is capable of further synthesis to produce ingrain colours is one of the essential features of solution as opposed to chemical action." Why this is so they do not, however, explain. It is even known (Dreaper, *J.S.C.I.* 13, 96), that in some cases this action of developing cannot take place. There seems to be as much evidence for, as against this proposition.

While arguing that dyeing is a matter of solution they hold that the molecular configuration of the reagents plays a part. One of the principal arguments against the solid solution theory is that solid solution is practically impossible when the varied nature of these reagents is taken into account.

Their contention, too, that the action is aided by the presence of salt-forming groups (chiefly OH), modified by the groups with which they are in proximate or immediate contact, at once brings us back to the chemical theory, and with this the need of a solid solution theory vanishes.

We here have a singular division of the action of dyeing; and solid solution relegated to the *product* to the exclusion of the process of dyeing, which may be either physical, or chemical.

The claim made by Weber that once grant a chemical action, and the solid solution theory is no longer required to explain the action of dyeing, seems a reasonable one. The claim that the substance in solid solution is different from the one in solution is an arbitrary one.

Weber contended that the differentation between the process of dyeing, and the final state of the dye "contains all the elements of a scientific abortion." Furthermore, that the writer's investigations, coupled with his own (above), lead to "an unconditional rejection of the solid solution theory as proposed by O. N. Witt."

It is of interest to note that S. E. Sheppard (*Photo. Journal*, 1903, 271) holds that the colour sensibility of silver haloids, when treated with certain dyes, is due to the formation of loose compounds of the dye and the haloid. The extra sensitiveness of these silver salts to the action of certain rays of light might be, in a way, comparable to the results obtained with primuline diazotised *in situ*.

The results obtained by Walker and Appleyard (*J.C.S.* 1896, 1334) with picric acid, and its distribution between water and silk, do not confirm

v. Georgievics' experiments with indigo carmine, or at any rate, do not agree with them.

In this case they found that

$$S/\sqrt[2.7]{W} = K.$$

Here we have a case where the simple rule is not followed, which it would be if the molecular state were the same in both solvents. The solid solution theory requires that the ratio of dye in solution to that in the fibre will be a constant irrespective of concentration.

If, however, the molecular weight is *n* times as great in the one solvent as in the other, then the *n*th root of the concentration in the first solvent will have a constant ratio to the concentration in the other solvent.

In the latter case

$$\sqrt[n]{CS}/CW = K$$

will apply.

Walker and Appleyard found that with picric acid and silk an equilibrium was established between the fibre and solution (dyeing at 100° C.).

Also, if the dyed silk was treated with successive baths of water the action was reversible, but the time taken to reach a state of equilibrium was much longer (seven hours). It did not matter if the dye was on the fibre or in the solution, a constant ratio was ultimately obtained.

The result does not necessarily uphold the solid solution theory. It is equally in agreement with any theory which requires a state of equilibrium, be it physical, or chemical.

The law of the distribution of picric acid at 60° C. was found to be

$$S/\sqrt[2.7]{W} = 35.5$$

This result does not give support to the solid solution theory, for it indicates that the molecule of picric acid in solution is 2.7 times as great as the molecule "dissolved" in the silk.

The freezing-point and electrical conductivity determinations indicate that picric acid is present in water in a simple molecular state. Therefore, so far as our knowledge goes, it is impossible to reconcile these figures with any theory of solid solution.

By a mathematical transformation of the above formula we obtain

$$\log S = \log 35.5 + \frac{1}{2.7}\log W.$$

which when differentiated becomes

$$\frac{dS}{S} = \frac{1}{2.7} \cdot \frac{dW}{W.}$$

This indicates that if the concentration in the water is increased by any volume, the concentration in the silk will increase by $\frac{1}{2.7}$ of its own value.

Formulæ of this nature apply in many cases to absorption phenomena. Schmidt and Küster have shown this to be the case (*Annalen*, 283, 360).

By substituting alcohol for water in these experiments, in which picric acid is more soluble, less was taken up by the fibre. The ratio of the two concentrations to produce the same shade remains fairly constant, and is nearly the ratio of the relative solubility of picric acid in water and alcohol at 60° C.

When benzene was used as a solvent, abnormal results were obtained. The silk would not take up any dye, in spite of the fact that rosaniline at once colours silk from this solution. Some peculiarity in the system is indicated here, or some joint property of the picric acid and benzene is possibly the cause of the different action. The difference between the dyeing action of picric acid in water, and benzene might be due to the fact that in the former it is said to be in a state of almost complete dissociation, and in the latter it is scarcely dissociated at all.

In this case it would be the H ions which influence dyeing, as sodium picrate will not dye at all. It is stated also that picric acid dissociates in alcohol.

Benzoic acid is readily absorbed by silk. A solution of this acid was dissociated to the extent of 6 per cent. The salts of this acid are also highly dissociated, and any addition of the latter to solutions of benzoic acid reduces its dissociation from 6 per cent. to zero. It would be expected that a smaller percentage of acid would be absorbed under these conditions. The absorption is actually reduced from 17 per cent. to 1.5 per cent. The reaction does not hold however for alkaline benzoates.

Further experiments with other weak acids did not corroborate these results. No relation could be traced between the relative rate of dissociation as measured by the presence of H ions in solution, and the relative rate of absorption by silk. If, however, the acids be divided into the two classes of aromatic and fatty acids, a much closer agreement exists between the constants.

The average absorption of the aromatic acids was 23 per cent., that of the fatty acids 5 per cent. In most cases the proportion of acid absorbed to acid in solution bears an almost constant ratio, yet in some cases the absorption increases rapidly as the acid becomes more dilute. With citric acid the action is abnormal. The amount taken up by the silk is almost independent of the concentration, and is constant in amount.

These results seem to indicate that a solid solution theory is unsatisfactory. Solid solution was originally defined by van't Hoff (*Zeit. Phys. Chem.* 1890, 5, 322), as being a "solid homogeneous complex of several substances, the proportions of which may vary without affecting the homogeneity of the system."

Schneider (*Zeit. Phys. Chem.* 1895, 10, 425) suggested that when barium sulphate carried down ferric sulphate from its solution, the action was of this nature, although he noticed that the ferric salt carried down was proportional to the amount of the insoluble barium compound present, up to the limits of occlusion. Beyond this point the presence of excess of iron salt in the solution had no effect.

More recent investigators do not seem to agree with this suggestion. Jannasch and Richards (*J. pr. Chem.* 1889, 39, 321) consider the action to in some way involve chemical action, rather than solid solution. Ostwald and others seem to agree with this view of the case. This subject received further consideration from Hulett and Duschak (*Zeit. Anorg. Chem.* 1904, 40, 196), who have further noticed that when barium chloride is absorbed in this way by barium sulphate, it is not necessary that the soluble salt be present at the time of precipitation. When finely divided crystals of the sulphate are suspended in the solution the same action takes place. They further consider that this phenomenon may be due to the formation of complex salts, such as $(BaCl_2)SO_4$ or $(H.SO_4)_2Ba$.

Quite recently Korte (*J. Chem. Soc.* 1905, 1508), as a result of further investigation of this subject, does not agree that solid solution is the cause of this action.

It is also known that barium sulphate will absorb metals from colloidal solutions of the same (Vanino and Hartl, *Ber.* 1904, 37, 3620). These absorption results with such a comparatively inert substance as barium sulphate will give the dyer an insight into the possibility of some such action taking part in the phenomena of dyeing, and lake formation.

These results suggest rather that "absorption" is possible under such conditions as are indicated, and that this is by no means confined to such conditions as approximate to those which obtain in the dye-house.

CHAPTER VIII

EVIDENCE OF CHEMICAL ACTION IN DYEING

THE suggestion that the dyeing action is primarily a chemical one, has received support in the past from many investigators who have brought forward evidence in favour of this hypothesis.

If it is possible to prove that the many and varied operations in dyeing and mordanting are governed by the laws which control ordinary chemical reactions, it is evident that our knowledge of the subject is at once put on a satisfactory and simple basis.

It is, therefore, of interest to follow closely the arguments, and facts, which have been recorded in favour of this view.

Unfortunately, the conditions under which much of the work on the subject has been effected are not entirely satisfactory. As a result, some of the data available are unreliable, and it is impossible to allot to some of the work its true value as evidence in favour of such action.

As early as the year 1737 Dufay drew attention to the possibility of the dyeing action being a chemical one. This view was also supported by Bergmann in 1776.

In these early days the relative affinities of different fibres for the same dye-stuff were considered to be evidence in favour of chemical action. Bergmann, for instance, specially pointed out that sulphate of indigo is attracted by wool in greater proportion than by silk. He attributed this to the greater attraction of the substance of the former fibre for the dye.

Wool was said to exert such an attraction for the dye that the dye-bath was completely exhausted. On the other hand, silk could only reduce the amount present in the dye-bath.

From this it is evident that these early investigators realised this factor in dyeing, viz., the attraction of the fibre for the dye; and in this way they differed from those who at this same period ascribed the action to purely mechanical phenomena. If it can be established that dyeing is primarily due to this cause, the subject is at once narrowed within definite limits.

Macquer in 1778, in his "Dictionnaire de Chimie," confirmed the idea that wool and all animal fibres are the materials which lend themselves most readily to the dyeing action. He stated that linen and all the vegetable fibres are the most difficult to dye, taking the least number of dyes, and holding them loosely. He placed silk in an intermediate position, not classifying it as a purely animal fibre. He did not deny that this variable facility of taking and retaining different substances is greatly due to the number, size, and arrangement of the pores, and their relative size as compared with the dye particles, but he did not allow that this is the only cause of the differences experienced in dyeing different fibres, and of the results obtained.

In support of this statement the following experimental evidence was advanced. If one-pound lots of wool and silk be mordanted with alum in excess, and dyed separately in a dye-bath containing cochineal, with one ounce of dye in each case, the wool will take a much darker colour. To obtain the same shade on the silk 2½ ounces of colour are necessary. In both cases the dye-bath is exhausted. This effectually disposed of the idea put forward by d'Apligny that the pores are smaller in the case of silk, and can only take the finest particles of dye. Dyeing, therefore, is not simply a question of encased particles. There is a real "adherence on contact," and even a chemical combination varying with the properties of the dyes and fibres entering into the reaction. He was of opinion that the effect of a surplus number of pores might even diminish the colour-effect by concealing the coloured particles. Dyeing was largely a question of surface action.

Berthollet in his "Elements of Dyeing" collected all the facts bearing on the subject, and favoured the chemical theory as a result of his investigations.

Chevreul also came to the conclusion that the action of dyeing was of the same order as chemical action, which takes place slowly, when two or more bodies are in contact.

Persoz, in criticising Crum's mechanical theory, held that the view that acetate of alumina is decomposed naturally by the cotton fibre, just in the same way as it would be if the fibre were absent, is untenable. He refused to believe that the same amount of alumina would be given up by the acetate in contact with mica plates. This difference would be still more marked at an elevated temperature. He therefore considered that the cotton fibre exerted a powerful influence on the decomposition of the aluminium salt. (*See* p. 143.)

He actually gave particulars showing, in the case of alum solution, that actual decomposition of the solution took place when cotton or silk was in contact with it. He recorded that the solution became more acid, owing to its being deprived of a notable amount of its base.

These experiments are probably the first of a series dealing with the decomposition of salts in solution by fibres. They may be regarded as the first direct indication that the action might be a chemical one. Macquer's results might have been due to mechanical, or even optical causes, but this experiment stands on a different basis, and the proof of chemical action was thought to be a convincing one.

These results do not agree with Crum's contention that the rate of change in a solution of acetate of alumina is the same whether a fibre be present or not. Persoz also asked how the colour mixed with so viscous a solution as gum or starch can occupy these sacs expelling the air and taking its place in the printing of fabrics.

He stated also that a fibre impregnated with manganese dioxide should not dye, yet it is in a very favourable state to take up indigo. The fact that some substances, such as baryta, calcium sulphate, &c., are never fixed by the fibre, while others are, is, he claimed, in favour of the chemical theory.

Muspratt (" Chemistry as applied to Arts," p. 766) thought that compounds deposited on wool or cotton became fixed through different causes. " Wool is strongly contracted by acids, and it is only under their influence that we can fix colours upon it. Cotton is contracted by alkali, a colour adheres to it only in so far as it presents an alkaline reaction." The idea was also advanced that the different colours assumed by wool, silk, and cotton with the same dye, were due to configuration of the fibres.

Kuhlmann (*Compt. Rend.*, April 1856) dyed samples of cotton and linen which had been nitrated, and noted the results obtained. The pyroxylin was well washed with water, and ultimately with soda. After mordanting and " ageing," samples of these materials were dyed. All the nitrated fibres gave excessively pale shades, as compared with the natural fibres. There seemed to be evidence that although the treated fibres rejected the mordants, yet they had increased attraction for the madder itself. Similar results were obtained with Prussian blue.

To obviate the possibility of these results being due to physical alteration in the fibre, he used Béchamp's process to denitrate the fibre, and noted that the cotton immediately recovered its property of receiving mordants and colours. The effect of varying the degree of nitration was to give varying results. He extended those experiments to wool, silk, hair, &c.

It was also noticed that picric acid gave a very strong tint on nitrated cotton.

Kuhlmann concluded that the chemical composition of the bodies to be dyed had the greatest influence upon the dyeing; also that dyeing is due to chemical combination, and that the effects due to capillarity, and the peculiar structure of the material, were of secondary importance.

It may be pointed out that the early authorities who favoured a chemical theory, based their theoretical conclusions on the hypothesis that the dyeing action was similar to, say, the reaction between caustic soda and hydrochloric acid. In other words, that it was a definite, and simple one.

It is assumed to-day by those who favour chemical action, that the animal fibres possess acid and basic properties. They therefore combine with and fix the dye-stuff, at least those which possess either acidic or basic properties themselves. We may therefore get actual salt formation.

The fact that the animal fibres contain amido-acids is therefore the basis of this theory. The fibre substance therefore contains both amido and hydroxyl groups, which play their part in the respective cases where basic and acid dyes are used.

These two species of dyes might even be dyed on a fibre already mordanted and dyed with alizarine the lake of which would be held mechanically. The mordant in this case would also be attracted chemically, and then by double decomposition, or otherwise the lake would be formed.

The statement has been made that " there is no colouring-matter which does not possess either acid or basic properties" ("Manual of Dyeing," page 8).

The first time that the idea was put forward that wool plays the part of an acid in the dyeing of basic dyes (magenta) was in 1884 (*J.S.D. and C.* 1, 209), when Hummel likened the action of the fibre to the fixing action for dyes of oleic, or tannic acid on cotton, &c. Although Hummel did not state in terms the decomposition which must take place when a basic hydrochloride combined with the wool substance in this way, yet it is clear that the hydrochloride must split up in order to enable the base to combine with the acid.

In the case of wool it was afterwards pointed out by Knecht (*J.S.D. and C.* 1888, page 72), that when this fibre is dyed with basic dyes (hydrochloride), that the whole of their acid is left in the solution.

If the amido theory is correct, it is difficult to explain why the acid does not combine with the fibre. The writer doubts if the same result would be found with silk when the affinity of that fibre for acids is considered.

Hummel also claims that this action is visible to the eye. When a colourless rosaniline salt is used, the fibre is coloured magenta.

It is claimed ("Manual of Dyeing," p. 8) that this conclusively proves the chemical theory, and that a coloured salt is formed with one of the constituents of the fibre.

If the action is a chemical one, it will follow that a point will be reached when the fibre substance will all be used up, and a point of maximum absorption attained. The following experiments are put forward by Knecht and Appleyard (*J.S.D. and C.* 1889, p. 74), to prove that this is the case. Silk was dyed with a large excess of picric acid and naphthol yellow respectively, with the following results.

	Picric acid.	Naph. Yel. S	Tartrazine.
Amount fixed . .	13.2%	20.8%	22.65%
Do. in solution .	37 0%	29.2%	27.35%

Fifty per cent. of dye was taken in each case on the weight of the fibre dyed. The ratio taken up of Naphthol Yellow to picric acid 20.8/13.2 is in the ratio of their molecular weights.

Tartrazine does not seem to follow this law, however. As picric acid contains one OH group, Naphthol Yellow one OH and one SO_3Na, and tartrazine 2CO.OH and $2SO_3Na$ groups, it is difficult to decide in what way they might, or might not, combine with the fibre substance.

Von Prager and Ulrichs (*Farb. Zeit.* 1891, 373) hold that these results are unreliable, and v. Georgievics denies that the Naphthol Yellow and picric acid are taken up in molecular proportions.

Recently (*J.S.D. and C.* 1904, p. 242), Knecht has brought forward results which he contends add support the chemical theory.

By an improved method of analysis and working with pure dyes, the following absorption results were obtained:

Dye used.	Amt. used.	Taken up.	Calculated.
Orange G. . .	50%	16.24%	—
Crystal Scarlet .	50%	18.23%	18.02%
Scarlet 2 G. . .	50%	16.37%	—
Xylidine Scarlet .	50%	17.12%	17.30%
Orange G. . .	25%	15.68%	—
Crystal Scarlet .	25%	17.42%	17.40%
Scarlet 2 G. . .	25%	15.53%	—
Xylidine Scarlet .	25%	16.22%	16.40%

Orange G., Atomic wt. 452, Crystal Scarlet 502,
Scarlet 2G. 452, Xylidine Scarlet 479.

Picric acid is now said to act in an abnormal way, and not in the way originally stated. In dyeing wool with increasing amounts of dye-stuff, a limit of absorption is reached in each case.

For instance, with Crystal Scarlet the following results were obtained:

Percentage of colour used:
50 25 22.5 20 17.5 15 12.5 10 7.5 5.0 2.5
Percentage of colour taken up by fibre:
18.2 17.3 17.0 16.6 15.3 14.2 11.9 9.6 7.2 4.7 2.2

This author holds that these experiments favour a chemical theory, from the fact that the dyes are taken up in molecular proportions.

The effect of excess of acid in dyeing is said to be due to the production of degraded products in the fibre, which resemble lanuginic acid in their chemical action.

The fact that the water can be varied, within limits, without altering the percentage of dye taken up is held to disprove the solid solution theory. If this is so, and with such a definite chemical action as is claimed, the fact that up to the point of saturation the dye is not all removed from the liquid would seem equally to point against a chemical action on the old hard and fast lines.

The law of mass action might possibly influence the result however.

Alizarine S. (powder), oxalic acid and alum can be boiled together indefinitely without combination or at any rate, any visible change. If lanuginic acid, said to be present in wool, is added, a bright scarlet precipitate is formed. This is said to give additional evidence in favour of the chemical view.

As before pointed out the above ratio breaks down entirely in the case of the sulphonic acids of phenols and amines. Dehydrothiotoluidinesulphonic acid is readily absorbed by silk, yet Prof. Green could not find any of the above which had an affinity for the animal or vegetable fibres. It is very difficult to explain why these sulphonic acids are not attracted by the animal fibres. The amido acid theory requires that they shall be readily absorbed. If the animal fibres have in their substance a compound which readily combines with acid compounds, the only explanation of the above is that soluble compounds are formed.

In the case of wool very little dyeing action takes place in a simple solution of these dyes in water. No figures are available for silk. If, however, an acid be added to the solution the colour acid is set free, and rapidly dyes the fibre, in the case of silk at ordinary temperatures.

A preliminary treatment of wool with sulphuric acid, followed by very thorough washing, will cause this fibre to dye rapidly, when introduced into a neutral solution of an acid dye in the form of its sodium salt.

It is claimed that this can be satisfactorily explained by assuming that the wool fibre has affinity for the acid, and retains sufficient to set free the colour acid. It would seem, however, that this explanation is not altogether satisfactory.

An addition of sulphuric acid over and above that necessary to decompose the dye acid salt has an altogether abnormal effect on the rate of dyeing. If the dyeing action is a strictly chemical one, the excess of sulphuric acid might be expected to have the opposite effect. The nature of this reaction is well illustrated by the following experiment. Boiling in distilled water will partly remove the dye (colour acid) from a silk skein. If then a few drops of a strong acid are added to the solution nearly all the colour will return on to the fibre.

It is difficult to understand this action from the chemical point of veiw. In what form is the re-dissolved colour in the solution? If present as free acid, why should the addition of acid influence the result? If, on the other hand, the colour acid fibre compound is not decomposed, but dissolves out in the hot water, can the conditions exist under which this fibre compound is decomposed on the addition of acid, the colour acid set free, and the latter combine to form the *same compound* in the fibre again in the presence of the acid which has decomposed it in the solution? The opposite effect might be expected, viz., that the sulphuric acid would partly replace the colour acid. This matter seems to deserve special attention.

It is contended that the substances in the animal fibres which produce these dye lakes or compounds can be isolated.

Prof. Liechti states that albumin will decompose a basic dye in much the same way as an animal fibre. In this case also, the acid remains in the solution. It will be remembered, however, as mentioned elsewhere, that this decomposing action is not confined to organic compounds of animal origin, but may take place with such inert substances as porcelain. It is claimed for the above reaction that "here there can be no doubt that chemical combination takes place, as the coagulated albumin is dyed magenta."

The proof here is not more satisfactory than it is in the case of magenta-dyed wool. In order to uphold such a statement it is necessary to ignore the general reactions obtained with substances of the above nature.

Knecht states that if wool, or silk, be dyed with night blue, and the dye subsequently extracted with alcohol, the compound actually formed between the dye and the fibre is extracted. If this solution be treated with barium hydroxide, the night blue is precipitated, and the fibre substance can be recognised in the solution.

This has been denied (*Zeit. fur Farb. und Text. Ch.* 1903, 215), it being maintained that no such action will take place if the wool is purified with alcohol before dyeing. The organic matter extracted is not of the nature stated, but consists of substances extracted by alcohol alone.

This criticism has been answered (*J.S.D. and C.* 1904, 72), by Knecht repeating his experiments after a preliminary treatment with alcohol. Under these conditions he states that he obtained a yellow residue, smelling of burning wool after ignition, and precipitated by an aqueous solution of night blue, or magenta. It would have been more satisfactory if a blank experiment had been made side by side with the night blue one, in addition to the preliminary purification.

At first sight the case for the chemical theory seems to receive support from the action of nitrous acid on the fibre, and subsequent development with phenols, &c. There does not seem to be any doubt as to the action in this case. The silk shows by its altered colour that the nitrous acid has acted on it and the subsequent development with phenols, or amines, is rapid and startling in its nature. It is certainly the case that some constituent of the fibre actually enters into the reaction, which produces these "dyes." An attempt made by the writer to isolate these compounds was not very successful. They seemed to be present in very small quantities.

No other experiments seem to afford such a clear indication that chemical action *may* take place in the process of dyeing. It might be fairly argued that the dyeing action is of a strictly chemical nature, if the matter rested here.

Unfortunately, these experiments and their influence on the action of dyeing have been discounted by some experiments of Bentz and Farrell (*J.S.C.I.* 16, 405). After confirming the above reactions, and that silk contains amido groups, the fibre was treated with nitrous acid for thirteen hours. After washing the fibre was boiled with alcohol, or an acid solution of cuprous chloride. This removed the amido groups. The fibre would not then rediazotise. The NH_2 (or NH) groups had been removed. From the chemical point of view it is, therefore, clear that the fibre should not dye under these conditions. But the "deamidated" fibre takes acid colours equally as well as the original fibre. Therefore, the inference is drawn that the amido groups play little or no part in the dyeing of silk (or wool) with acid colours.

These experiments need to be extended; they should cover the subsequent resistance against soap, water, and alcohol. This should show if the amido groups play any secondary part by holding the dye when it is once on the fibre.

The writer (*J.S.C.I.* 13, 96) gave the results of a number of experiments on dyes dyed direct and ingrain respectively. Figures are given, showing by curves and tables the differences obtained by dyeing primuline colours "direct" and "ingrain" on silk.

Their fastness against soap and alkali solutions at a high temperature, was taken as a comparative measure of the way the dyes are held by the fibre. A standard solution of neutral soap, or sodium carbonate was used in all cases.

The general results obtained were as follows:

The difference in fastness of the dyes when dyed "ingrain" and direct was very noticeable. This is clearly shown in the series of curves accompanying the paper.

The dyes when dyed direct were not so fast as the original primuline against soap solution.

The developed amine dyes are, with one exception, very much faster in their resistance to soap than the corresponding alcoholic or phenolic dyes. It may be argued from this, either that the fibroin shows a stronger acid than basic reaction, as measured in this way, or that the solvent action of the soap is greater in the case of the alcoholic dyes than in the other. Either of these explanations is possible.

It will be noticed that in the one case given of an azo triple dye, that the resistance against soap is increased in the ratio of 1.7 to 1. This may, again, be due to increased molecular volume, or to a state of greater insolubility. It would have been interesting to have used a phenol in the case of the second development, and also to have dyed the azo dye direct, and noted the effect of one or two developments on the fastness against soap. The only possible comparison given is that of Atlas Red R developed with β-naphthol. This dye is prepared by diazotising primuline, and combining with *m*-tolylenediamine.

This dye was not so fast as might be reasonably expected. It was argued from these figures that the relative fastness of these two classes of developed dyes was not so much due to internal molecular structure as to the phenolic, or basic nature of the dye.

Some "developers" will not act on the diazotised primuline on silk. β-naphtholsulphonic acid (R salt) is an example. This can hardly be due to a simple matter of diffusion of the developers, for substances (dissolved) which are present in the ratio of their molecular weights, exert equal pressure at the same temperatures.

If this is so, it should be easily confirmed by nothing the relative amount of the "developers" absorbed by equivalent solutions. An alternate suggestion is that the diazotised primuline has an affinity for this silk fibre which the R salt cannot overcome. The presence of a sulphonic acid group in the developer may influence the reaction, and also the solution state of the developer.

The fact remains, at any rate, that the R salt is unable to combine with the diazotised primuline in a silk fibre, but able to do so in a cotton one.

The relative rate of development with R salt on cotton and mercerised cotton where the fibre is in a higher state of hydration might throw further light on this subject.

The relative amounts of dye taken up under standard conditions from soap solution do not seem however, to indicate that the fibre has much chemical influence on the amount of dye absorbed by the dye, as the following table taken from my paper (*ibid.*) will show.

Dye.	Per cent, of dye taken up by fibre.
Primuline and $C_6H_5.OH$ . .	0.18
,, ,, $C_6H_5NH_2$ . .	0.19
,, ,, $C_6H_4(NH_2)_2$.	0.11
,, ,, $\beta C_{10}H_7.OH$.	0.12
,, ,, $C_6H_4.COOH.OH$	0.11

The table on p. 198 shows the result obtained in the experiments by boiling for different times in standard soap solution, and covers most of the developers used in practice.

The samples of silk were dyed with the equivalent quantities of the dyes, or equivalent propor-

Dye.	Developer.	5 Min.	10 Min.	15 Min.	30 Min.	45 Min.	60 Min.	Remarks.
Primuline	C_6H_5OH	—	0.05	0.10	0.15	0.18	0.20	— — Ingrain.
,,	,, ...	0.40	—	0.50	0.57	0.65	0.74	— — Direct.
,,	$C_6H_4(OH)_2(1.3)$ . .	0.03	—	0.05	0.09	0.15	0.17	— — Ingrain.
,,	,, ,, . .	0.45	—	0.50	0.58	0.65	0.75	— — Direct.
,,	$\beta C_{10}H_7.OH$ . . .	0.02	—	0.05	0.10	0.13	0.15	— — Ingrain.
,,	,, . . .	0.30	—	0.40	0.50	0.55	0.63	— — Direct.
,,	$NH_4.OH$ . . .	0.02	—	0.04	0.05	0.06	0.08	— — Ingrain.
,,	,, ...	0.24	—	0.36	0.42	0.46	0.50	— — Direct.
,,	$C_6H_4.COOH.OH(1.2)$.	0.03	0.04	0.05	0.07	0.09	0.12	— — Ingrain.
,,	,, ,, .	0.48	—	0.60	0.68	0.71	0.75	— — Direct.
,,	$C_6H_5.NH_2$ . . .	0.04	—	0.05	0.06	0.09	0.10	Azo dye. . Ingrain.
,,	,, . . .	0.40	—	0.50	0.60	0.65	0.70	,, . . Direct.
,,	$C_6H_5.NH_2$ . . .	0.01	—	0.03	0.04	0.05	0.07	,, (Na CO) Ingrain.
,,	,, . . .	0.18	—	0.20	0.25	0.28	0.30	,, ,, Direct.
,,	$C_6H_5.NH_2$ . . .	0.01	—	0.02	0.03	0.04	0.05	Azo triple dye Ingrain.
,,	,, . . .	0.38	—	0.45	0.45	0.58	0.61	Direct.
,,	$C_6H_4.(NH_2)_2(1.3)$ . .	0.01	—	0.025	0.035	0.05	0.052	— — Ingrain.
,,	,, ,, . .	0.40	—	0.45	0.55	0.65	0.80	— — Direct.
,,	$\beta C_{10}H_7.NH_2$ . . .	0.10	—	0.15	0.20	0.25	0.27	— — Ingrain.
,,	,, . . .	0.50	—	0.60	0.65	0.70	0.79	— — Direct.
,,	— — —	0.10	0.20	0.30	0.39	—	0.60	— — Direct.
Atlas Red R	$\beta C_{10}H_7.OH$ . . .	0.10	—	0.14	0.20	0.25	0.27	— — Ingrain.
	,, . . .	0.50	—	0.55	0.62	0.71	0.76	— — Direct.

tions of primuline. The conditions of dyeing were kept constant in all cases. After drying the sample lots of silk were boiled out for the periods indicated, and the resulting shades were carefully compared with standard samples; or else the dye in the soap solution was estimated by colorimetric methods. In this way, the loss of colour on boiling off was estimated with a sufficient degree of accuracy.

The ratio of colour removed in the case of these

Dye.	Developer.	"In-grain" x.	"Direct" y.	$\frac{x}{y}$	Remarks.
Primuline	$C_6H_5.OH$	0.20	0.74	$\frac{1}{3.7}$	
,,	$C_6H_4(OH)_2(1.3)$	0.17	0.75	$\frac{1}{4.4}$	
,,	$C_6H_4.OH.COOH(1.2)$	0.12	0.75	$\frac{1}{6.2}$	
,,	$C_{10}H_7.OH\beta$	0.15	0.63	$\frac{1}{4.2}$	
,,	$NH_4.OH$	0.08	0.50	$\frac{1}{6.2}$	
,,	$C_6H_5.NH_2$	0.10	0.70	$\frac{1}{7.0}$	Azo dye.
,,	$C_6H_5.NH_2$	0.05	0.61	$\frac{1}{12.0}$	Azo triple dye.
,,	$C_6H_5.NH_2$	0.07	0.32	$\frac{1}{4.6}$	Na_2CO_3
,,	$C_6H_4.(NH_2)_2(1.3)$	0.052	0.80	$\frac{1}{15.4}$	
,,	$C_{10}H_7.NH_2\beta$	0.27	0.79	$\frac{1}{2.9}$	
,,	$C_{10}H_7.OH\beta$	0·27	0.76	$\frac{1}{2·9}$	

dyes is seen in the table on p. 199. The influence of the solvent (soap, or sodium carbonate) seems to alter the rate of "boiling out" materially.

It is very difficult to reconcile these results with any purely chemical, or solid solution, theory. The stumbling-block is the altered fastness of dyes dyed ingrain and direct, and the indication that the dyes may be fixed in two ways. The difference between the fastness of the phenolic and amine dyes respectively may be explained in other ways.

The affinity of these dyes from primuline for cotton seems to vary greatly, and here again the metaphenylenediamine colour has a fair affinity for this fibre, and the beta-naphthol one very little. These results are obtained when dyeing this fibre direct. It is therefore quite clear that a difference in dyeing properties is apparent when amines are used in place of phenols in the production of these dyes.

Another point of importance was indicated. It was shown that the colours produced in the two cases, direct and ingrain, were not identical in shade, as shown in the table on p. 201.

This might indicate some difference either in the action or state of the dye. This has since been suggested by Brand (*Proc. Soc. Ind. de Mulh.*, Feb. and April 1901) as being due to a secondary action between the diazo compounds and the wool. In my paper I indicated that the fact that some developers would not act on the diazotised primuline might be taken as a possible proof that there was some action between the diazo compound and the fibre. The same explanation has more recently been put forward by Hepburn (*J.S.D. and C.* 1901, 279).

Taking the case of para-nitraniline, the fastness of the dye against washing is said by Brand to be due to the paranitrodiazobenzene being partially reduced at the expense of the fibre substance to para-nitraniline. The excess of diazo compound would react, forming dinitrodiazoamidobenzene. This substance is very insoluble.

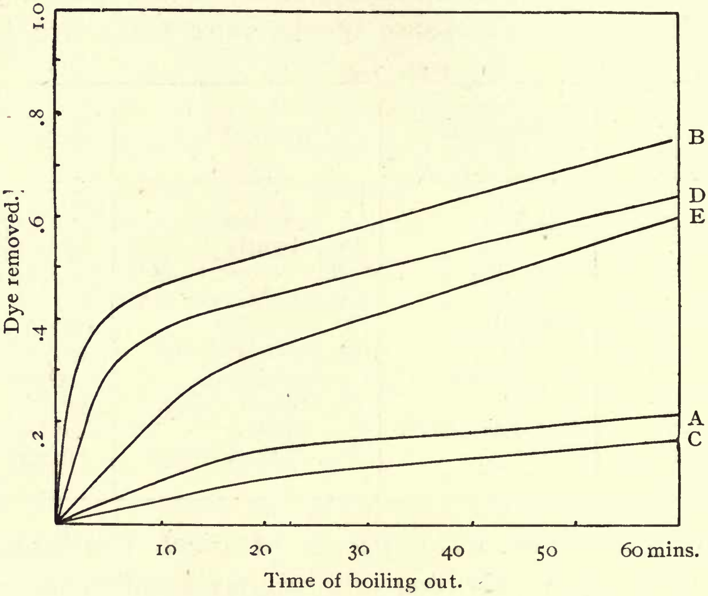
Dye.	Developer.	Colour obtained.	Method of dyeing.
Primuline	$C_6H_5.OH$	Yellow.	Ingrain.
,,	,,	Do., slightly darker.	Direct.
,,	$C_6H_5.NH_2$	Yellow (brown shade).	Ingrain.
,,	,,	Do., slightly darker.	Direct.
,,	$C_6H_4(OH)_2$1.3	Orange.	Ingrain.
,,	,,	Do., redder shade.	Direct.
,,	$C_6H_4(NH)_2$1.3	Red-brown.	Ingrain.
,,	,,	Do., redder shade.	Direct.
,,	$C_6H_4.OH.COOH$	Yellow.	Ingrain.
,,	,,	Do., slightly duller.	Direct.

It is just possible that a similar reaction may take place in the case of diazotised primuline, and that it is this compound which is so sensitive to light, but it is not so easy to explain the subsequent action of the developers.

It is held by Rossi (*Rev. Gen. Chem.* 1901, 670) that silk will also act on diazo compounds as a reducing agent, diazoamido or azoamido compounds being formed, the difference being determined by the stability of the diazoamido compounds. This reaction once ended, the resulting compounds are held mechanically by the fibre.

The reduced action of some developers may,

Resistance of Phenolic dyes to the action of soap. (Dreaper.)



FASTNESS OF INGRAIN COLOURS.

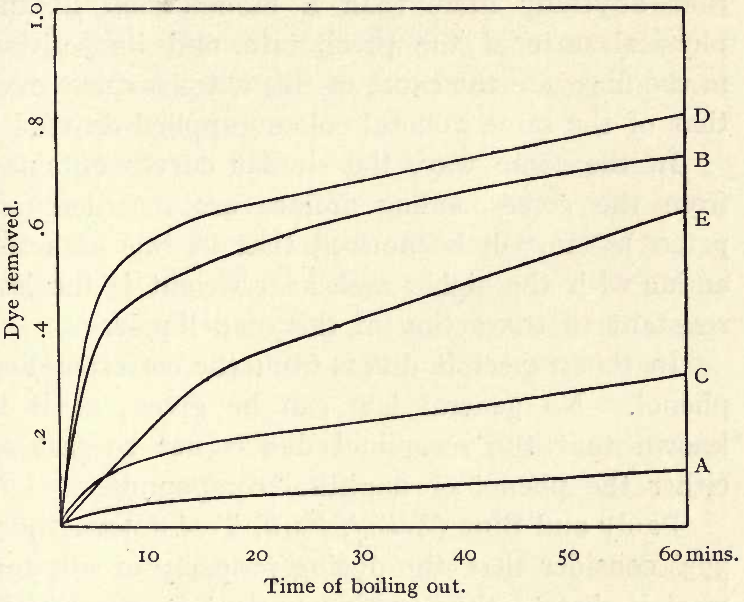
A: $C_6H_5.OH$ (ingrain). B: do. (direct). C: $C_{10}H_7.OH\beta$ (ingrain).
D: do (direct). E: Primuline (direct).

however, be due either to the diazo compounds being held by the fibres by some secondary chemical action, or else to the molecular aggregates of these developers being too large to enter the fibre substance in the form in which they are present in the solution.

If some such reducing action takes place as is indicated when these dyes are developed in silk, what is the corresponding action in the case of cotton ?

The curves drawn from the above tables (*see* p. 202) will also illustrate the relative resistance of the phenolic dyes towards the action of the standard soap solution. They show the general results which may be expected in practice, and the relative fastness of the dyes.

Resistance of Amine dyes to the action of soap. (*Dreaper.*)



FASTNESS OF INGRAIN COLOURS.

A : $C_6H_5.NH_2$ (ingrain). B : do. (direct). C : $C_{10}H_7.NH_2\beta$ (ingrain). D : do. (direct). E : Primuline (direct).

The extra fastness of the ingrain dye in the case of, say, cotton fibre and the phenolic dyes after a treatment with soda is certainly difficult to understand, from a purely physical point of view. Mineral colours, however, which are "developed" or formed on the fibre are certainly more resistant to the action of such solutions, and it is not likely that anything more than a modification in the physical state of the precipitate, and its position in the fibre, are the cause of this extra fastness over that of the same mineral colours applied direct.

In the same way, the similar curves obtained from the corresponding amines are recorded (*see* p. 203). It will be noticed that in this case the amine with the higher molecular weight is the less resistant to the action of the soap liquor.

In this respect it differs from the corresponding phenol. No general law can be given, as it is known that the resorcinol dye is not so fast as either the phenol or naphthol compounds.

Pauly and Binz (*Zeit. f. Farb. Text. Chem.* 1904, 373) consider that the dyeing property of silk and wool is due to the tyrosine present in albuminoid combination, and that it reacts by virtue of its phenolic character. Pure tyrosine gives similar results, but some albuminoids like salmine and scombrine, do not react in this way. Silk reacts (dyes) better than wool, because it has more tyrosine in its composition in the ratio of 10 per cent. to 3–3½ per cent.

It is not clear, however, that silk does dye better than wool. It is generally acknowledged that the reverse is the case. Silk may dye more readily, it is true, but these authors do not attempt to show that a standard dye will be taken up in the ratio of 10 to 3.5 at the saturation-point by the two fibres, which should follow if this theory is correct.

The presence of tyrosine in the silk fibre is indicated as follows. This fibre gives on oxidation an indophenol or oxazine reaction in a similar way to that obtained with a mixture of a *p*-diamine and a phenol.

If silk be soaked in a .05 per cent. solution of dimethyl *p*-phenylenediamine in the presence of acetic acid and sodium acetate, and bromine water added, the silk fibre takes a slate grey colour. In the absence of silk (or wool) no such colour is produced. This reaction takes place with tyrosine itself.

1.4 amidonaphthol will react in the same way. Erdmann's patented process for dyeing feathers, &c., is based on this reaction.

Some evidence brought forward by Knecht (*J.S.D. and C.* 1902, p. 103) complicates, and in a way tends to disprove the amido-acid theory.

The substances he isolated from wool and silk dyed with night blue would only combine with basic dyes, and not with acid ones. He also separrated a compound from silk which was stated to combine only with acid dyes.

The results obtained up to the present time by different investigators may be summed up as follows.

Colours may be obtained by treating silk and wool with nitrous acid, and phenols or amines, Therefore, silk or wool *may* be dyed in this way. Deamidated fibres can be dyed as well as the original ones, so that the dyeing property of silk or wool is not necessarily due to NH or NH_2 groups.

The relative action of the diamine colours on animal and vegetable fibres is difficult to understand, when considered from the chemical point of view. For instance, cotton may be dyed black, and wool be left white on dyeing in the cold with Diamine Black, BWH.

In a paper on the "Chemistry of Wool," M. Matthews (*J. Franklin, Inst.* CLIX., No. 5, 397) favours the amido-acid theory for the following reasons;

(1) NH_3 is among the products of destrutcive distillation of wool.

(2) Wool is easily hydrolised by dilute alkaline solutions.

(3) It readily combines with acids, and even with boiling dilute sulphuric acid.

(4) The nitrous acid reaction.

(5) The well-defined basic properties of the fibre.

The following so-called "coefficients of acidity" are given:

Wool	57
Silk	143
Albumin	20.9
Gelatin	28.4

All these facts may be readily allowed, but the evidence of the chemical nature of dyeing must ultimately rest on a more direct foundation, in view of the conflicting nature of the evidence, when it is considered from a general point of view, and is taken in conjunction with other recorded facts.

Even if the substantive colours owe their attributes to the grouping $>N-R-N<$ as held by Vignon, this theory is not applicable to many colours like primuline, the mono-azo dyes, &c., as pointed out by Green and Levy (*J.S.D. and C.* 13, 1898).

As far back as 1886 Möhlau attributed the substantive qualities to the alleged fact that benzidine could be extracted from its solutions by bleached cotton.

The above authors show that no affinity exists between benzidine and the cotton fibre, or even mercerised cotton. Dianisidine hydrochloride gave the same negative results.

It is considered by Willstätter (*Ber.* 1904, 3758) that if the dyeing of wool is due to salt formation, the fibre as an optically active substance should be capable of transforming, or "splitting," a racemic dye-stuff into its optically active constituents.

No racemic dye-stuff being available, the hydrochlorides of atropine and homatropine were used in the experiments.

An examination of the alkaloids left in the bath still showed that they were in no way changed, and remained optically inactive.

The inference is that no salt formation takes place.

CHAPTER IX.

EVIDENCE OF CHEMICAL ACTION IN DYEING
(*continued*)

THE suggestion that dyeing is primarily due to chemical action rather than physical action has received the support of R. Hirsch (*Chem. Zeit.* 13, 432).

He assumed that "Knecht has established beyond doubt, that dyeing of animal fibres is a chemical process."

Such being the case there is no reason why dyes alone should be regarded as capable of absorption unless these compounds have something in common from a chemical point of view, which distinguishes them from other compounds. Nietzki has endeavoured to show that this is the case (*Chem. d. org. Farbst.*, 2nd ed.).

The difficulty in including the nitro bodies in such a scheme is evident. Nietzki meets this objection with the statement that nitrophenols have most probably a similar constitution to the nitrosophenols, which are now generally regarded as quinone oximes.

Hirsch does not, however, agree with this view. Experiments were made to ascertain if wool has any affinity for organic substances in general.

If wool is "dyed" with β-naphtholsulphonic acid R, the greater part of the sulphonic acid is absorbed, and resists the action of boiling water; when the wool is put into a solution containing diazobenzene, or diazoxylene, the corresponding colour is developed with ease.

The nature of the alkali added to the bath greatly influenced the rapidity of the development. With sodium carbonate the action was very slow. Similar results were obtained by producing Naphthol Green (Cassella) on the fibre. Naphthionic acid was fixed on wool in either acid or alkaline solutions.

On the other hand, sulphanilic acid combined with great difficulty with wool.

G. H. Hirst's statement that a benzidine sulphate solution boiled with silk, or cotton, contains all its sulphuric acid at the end of the experiment, is no proof that the benzidine is taken up by the fibre.

These experiments seem to indicate that wool will absorb organic substances of the nature of naphtholsulphonic acids, and that an acid state of the solution is more favourable for absorption than an alkaline one.

The fact that naphthionic acid is fixed by the wool in both acid and alkaline solutions is probably against a chemical theory. Sulphanilic acid (*p*.-amidobenzenesulphonic acid) is absorbed with great difficulty, and only in concentrated solutions.

Three years later, Binz and Schroeter (*Ber*. 1902, p. 4225) supported the chemical theory, but they did not admit that in all cases the fixation of substantive dyes is due to salt formation between dye-stuff and fibre.

The fact that certain acid dyes will dye wool and silk in the presence of either acid, or alkali (caustic alkali), and that there are basic dyes which will dye in strongly acid solutions, is against any simple theory of salt formation. It is clear that some other action is involved.

Azobenzene-*m.m′*-disulphonic acid and *p.*-azobenzenemonosulphonic acid will both dye wool in an acid bath. The "colours" will stand washing with water, but are instantly discharged by dilute sodium hydrate solution. These examples therefore conform to a salt producing theory. If, however, we dye with *p.*-hydroxyazobenzene we get an intense yellow in acid, neutral, or alkaline solutions. Salt formation is therefore unlikely in this case.

Again, *p.*-amidoazobenzene and *p.*-dimethyl amidoazobenzene dye wool an intense yellow in a solution containing a small proportion of acid. The same shade is obtained, however, if the proportion of acid is increased to 6, 12, 20, or even 120 molecules of acid to each molecule of dye.

Further experiments showed that the hydrochlorides of *m.m′*-diamidoazobenzene and tetramethyl-*m.m′*-diamidoazobenzene gave different results. After an addition of 6 to 10 molecules of hydrochloric acid to each molecule of base the wool remained quite white.

The following conclusions were drawn from the experiments. The groups NH_2 and $N(CH_3)_2$ in the meta-position to the azo groups, and the presence of the sulphonic acid groups impart to the chromogen dyeing properties which result in the formation of loose salts with the animal fibres.

A different state of affairs is assumed in the case where the OH, NH_2, or $N(CH_3)_2$ groups are in the para-position. In the latter case the dyeing properties cannot be overcome by the addition of alkali to solutions of the phenolic dye-stuff, or of acid to the basic substances.

Most of the substantive dyes for wool and silk contain the amido- and hydroxyl-groups in the ortho- and para-positions relatively to the chromophor, and can be regarded as giving quinone derivatives as isodynamic forms. When, however, these groups are present in the meta-position, quinone formation does not occur, and the dyeing is only a question of salt formation, and that of a loose nature.

In the other cases where true dyeing is said to take place, the action is probably due to a condensation in the nucleus between the dye-stuff and the fibre.

In answer to a severe criticism by v. Georgievics, which is noticed elsewhere, in which the conditions of the experiments are attacked, Binz and Schroeter they bring further evidence in support of their case (*Ber.* 1903, 3008).

Azobenzenecarboxylic acid is a dye-stuff in the same sense as the corresponding sulphonic acid, but it will dye only in neutral solution.

Again, *p*-.benzeneazo-trimethylammonium hydroxide dyes wool, but the colour is destroyed by the addition of hydrochloric acid in equivalent quantity to the dye-stuff fixed.

The fact that chrysoidine and Bismarck brown give darker shades in the presence of hydrochloric acid is noted in confirmation of the idea that *p*.-amidoazobenzene yields with the fibre a condensation product, and not a salt. It is therefore contended that azobenzenesulphonic acid and carboxylic acids, *m*-amidoazobenzenes and quaternary ammonium bases of the azo compounds dye with simple salt formation.

On the other hand, ortho- and para-amidoazobenzenes and most of the ortho- and *p*.-hydroxyazo compounds cannot give normal salts.

Here a condensation of the fibre substance with the quinoid nucleus of the dye-stuff is said to take place.

These experiments will require extending before such definite statements can be accepted. For instance, they do not agree with Prof. Green's results obtained with the sulphonic acids.

These authors still further defend themselves against a second criticism by v. Georgievics (*Ber.* 1904, 727). They deny that the neutral sodium salt of azobenzene-*p*.-sulphonic acid is capable of dyeing wool in neutral solution. They claim that the wool used must have contained free sulphuric acid.

They also consider that the fact that alcohol will remove the dyes from the fibre is not proof that there is no combination between the dye and fibre.

The solvent action may be due to decomposition of the fibre dye compounds first formed.

They do not seem to meet the statement that benzene will act in the same way. They also deny that picric acid is extracted by alcohol from wool after dyeing.

Many of the contradictory results obtained by different observers may be due to the different conditions of dyeing, fibre state, &c.

Hirsch's experiments might well be compared with the above in their general effect.

Examining the tinctorial values of the three isomeric hydroxyazobenzenes (*Zeit. f. Farb. und Text. Ind.* 1904, p. 177), Prager criticises the results obtained by Binz and Schroeter. He will not allow that dyeing may be a condensation in the nucleus between the quinoid dye-stuff, and the substance of the fibre.

The ortho- and para-hydroxyazobenzenes are capable of assuming the quinone type, but the meta-compound cannot apparently assume an isodynamic form. The meta-compound should therefore not act as a dye.

In practice it is found that the meta-compound will dye wool, as well as the para-compound. These results are held not to favour the condensation theory.

Collecting some of the facts recorded in this chapter and elsewhere, the conflicting nature of the evidence in favour of a simple chemical theory will be at once realised.

1884. Müller Jacobs. Amido-azobenzene will not dye cotton, di- and triamidobenzenes will do so.

1889. Ewer and Pick. Naphthylenediamines. Position of amido groups determines dyeing power on cotton (α_1 α_3 positive dyes).

1889. Hirsch. β-Naphtholsulphonic acid R. dyes wool. Naphthionic acid fixed by wool (acid or alkaline). Sulphanilic acid has very slight affinity for wool.

1894. Green. Colourless sulphonic acids have no affinity for animal or vegetable fibres. Dehydrothiotoluidinesulphonic acid an exception in the case of animal fibres.

Colour derived from metaphenylenediamine and primuline will dye cotton, that from β-naphthol will not.

1902. Binz and Schroeter. Azobenzene *m.m′*-disulphonic acid and *p.*-azobenzenesulphonic acid dye wool from an acid bath; *p.*-oxy-azobenzene dyes wool in acid, neutral, or alkali bath, *p.*-amidoazobenzene and *p.*-dimethylamidoazobenzene dye in acid bath of any strength.

Hydrochlorides of *m.m′*-diamidoazobenzene and tetramethyl-*m.m′*-diamidoazobenzene, dye wool in neutral solution, but not acid.

1903. Binz and Schroeter. Azobenzenecarboxylic acid and *p.*-benzeneazotrimethylammonium hydroxide will dye in neutral baths, but not in acid.

1904. Prager. *o.*- *m.*- and *p.*-hydroxyazobenzenes dye wool in acid solutions.

1904. Binz and Schroeter. The sodium salt of azobenzene *p*.-sulphonic acid is not capable of dyeing wool.

It will be at once seen that the reactions which take place in dyeing are, from a chemical point of view, of such a nature that it is difficult to appreciate their true value.

It is not easy to explain the action of some dye solvents on dyed mixtures of cotton and silk. It is well known that some dyes may be dissolved out of the silk fibre and not taken out of the cotton by a solution of ammonium acetate. In this way "shot" effects may be produced.

It is generally agreed that cotton is comparatively inert as an absorbent of dyes, yet under these conditions we have an enormously increased attraction as compared with silk. With these dyes we may even obtain black cotton and white silk.

A further study of the relative "absorption" of the dyes in the respective fibres under varying conditions may clear up this point, and will be considered.

In the year 1884 Bœttinger discovered a dye which he named Congo Red. He found that it possessed the then extraordinary property of dyeing cotton direct from aqueous solution as well as it dyed silk.

The whole subject of the action of these direct dyes on cotton (and other fibres) is little understood.

In a general way, there seems to be some connection between the constitution of the dye molecule and its action. It seems to be important that the amido-groups occupy the para-position, and that the ortho-positions be occupied by a hydrogen radical. The meta-position seems to have little influence in the dyeing or tinctorial properties.

The double chromophorous group $\begin{smallmatrix}-N=N-\\-N=N-\end{smallmatrix}$ in the tetrazo dyes seems to influence the dyeing in some way, but the presence of this group alone does not suffice to make the dye a " direct " one.

The primuline dyes do not contain this group, nor are they azo dyes at all.

They possess the chromophorous group $<^{S}_{N}>C$. Some dyes contain both this and an azo group; a dye of this nature is Cotton Yellow R.

It may be said here that the view of chemical action occurring in the dyeing of these colours is unsatisfactory so far as the dyeing of cotton is concerned. In fact, the advent of these dyes has been as unexpected, and revolutionary, from the theoretical as from the practical point of view.

The fact remains that there are many dyes which dye cotton direct under conditions which seem to exclude any chemical action.

In certain cases, the affinity of the cotton for the dye is so great that the bath is almost exhausted. This is so in the case of Diamine Fast Red F. In other cases a great proportion of the dye is left in the solution. The facts known about the dyeing of these dyes are incomplete. The dye in most cases is readily removed by water. This is, of course, noticed with other dyes on silk. The amount of dye taken up seems to vary with the concentration but no careful work has been done on this subject. The results could not fail to be interesting. The addition of neutral salts and their great effect on the rate of dyeing in solutions containing these substances is very instructive. Their action from a chemical point of view is difficult to gauge. The fact that these dyes are less soluble in the salt solutions possibly accounts for their action, and this fact seems to point to a physical rather than a chemical process. The fact also that these dyes will, when on the fibre, combine with or form lakes with the basic dyes seems to show that the dyes are not in combination with the fibre (Knecht, *J.C.D.* and *C.* 1886, 2).

The attraction of these dyes for wool and silk is also a strong one, as is seen when the test of resistance is applied to the action of the ordinary solvents (water, &c.).

The factor which operates in the case of cotton therefore seems to have a similar value in the dyeing of silk or wool.

A point which must be noticed is, that these dyes seem on the animal fibres to have a greater resistance to the action of light than the same colours on cotton.

It seems strange, also, that these dyes are taken up more readily in alkaline solutions by cotton, and more readily in acid solutions by silk.

Diamine Milling Black is even said to dye well in a solution containing 7 ozs. of soap and

1½ ozs. of soda to a gallon (*Text. Manuf.* 1901, p. 319).

In the practical dyeing of cotton three supplementary processes are used to increase the fastness of these dyes, viz., diazotising; treatment with metallic salts; or the "coupling" process. From their action it will be necessary to briefly describe them here.

Diazotising produces shades which are very resistant to the action of soap solutions at the boil, and sometimes to light.

After dyeing, the fibre is put through a solution of nitrous acid, subsequently washed, and "developed" in solutions of amines, or phenols.

In practice β-naphthol, *m.*-phenylenediamine or resorcinol are chiefly used as developers.

In the case of primuline, chloride of lime gives a very fast yellow if it follows the diazotising process.

The increased fastness produced by the treatment with metallic salts is also noticeable.

The shades are faster against the action of soap and light.

Treatment with copper sulphate, although it does not act so universally as was at first claimed, gives very satisfactory results in many cases.

Diamine Sky Blue F.F. is greatly increased in fastness. Diamine Brill. Blue G. is claimed to give as fast colours as vat indigo blue in this way.

At one time it was thought that treatment with copper sulphate would increase the fastness of all dyes.

Bichromate of potash gives greater fastness against soaping with Diamine Jet Black and Diamine Brown M.

Fluoride of chrome is also used with Diamine Bronze, Fast Red F., &c., to produce the same effect. Where the action is not that of a mordant it is obscure.

The process known as coupling has been already referred to. Here basic dyes are added to the bath and fixed by direct combination, or lake formation.

The difficulty attending the production of a satisfactory theory to explain the varied results obtained in the dyeing of cotton has been increased by the addition of still another class of dyes, viz., the sulphur dyes; it would, perhaps, be more correct to say by the extension of this class, for Cachou de Laval may be considered a member of this group.

These colours are produced by soaking the cotton fibre in a hot alkaline bath in the presence of sulphide of sodium.

The colours are developed and fixed by subsequent exposure to the air (oxidation).

The extra fastness of dyes produced in the fibre is generally noticeable.

In this case the dye is soluble in the alkaline bath by reduction, and subsequently by oxidation insoluble dyes are produced in the fibre itself. In some cases a more energetic oxidation is necessary. Immedial Blue C. may be developed by hydrogen-peroxide or by the combined action of steam and alkali.

Until we know more about the constitution of these dyes it is only possible to speculate as to the exact nature of their development.

In the dyeing of indigo, also, some similar action plays at least a secondary part. Indigo is present in the dye vat in a soluble and reduced form. Subsequent oxidation of the indigo white after absorption in the fibre produces the insoluble indigo *in situ*. The dye so formed is remarkably fast against the action of light, or soap solution. It may, however, "rub" badly if the operation of developing is improperly conducted.

So far as we know we can reproduce the conditions of formation of these "oxidation" dyes as they exist in the presence of a fibre. There is no reason to think that the formation of the insoluble dye-substances in the fibre material takes a different course to that taken in solution, in the above cases.

The action of tannic acid on organic colloids is an instructive one. The tanning of leather is of such a nature, that the theoretical work connected with tanning should be closely followed by those interested in the general operations of dyeing.

The nature of the attraction which silk exhibits for tannic acid is indicated as follows. It is more readily removed from the fibre by a dilute solution of hydrochloric acid than by a solution of sodium carbonate.

The reaction between oxycellulose and basic dyes has been studied by Vignon (*Compt. Rend.* 125, 448).

It is found that this substance has a greater attraction for these dyes than the unaltered cellulose. This will be seen in the following table, which gives the results obtained with one gramme of fibre.

Fibre,	Safranine,	Methylene blue,
Cellulose	.000 g. absorbed	.002 g. absorbed
Oxycellulose	.007 g. ,,	.006 g. ,,

The same investigator (*Compt. Rend.* 1887, 125, 357) has made an attempt to determine the molecular groups which confer on certain dyes the property of dyeing cotton direct. Compounds having similar constitutions to these dyes were taken. The basic substances were employed in the form of their hydrochlorides, and their action in the presence of cotton carefully noted.

The following table shows the relative absorption of a number of organic substances.

Substances absorbed by cotton,	Neutral bath,	Alkaline bath,
Ammonia	.2–.4	.2
Hydroxylamine	.0–.3	.2
Hydrazine	1.2	1.7
Phenylhydrazine	3.6	2.9
Aniline	.1	.1
Dimethylaniline	.0	.0
Diphenylamine	.4	.4
o.-Phenylenediamine	.4	.6
m -Phenylenediamine	6.4	2.4
p.-Phenylenediamine	6.7	3.2
Benzidine	6.0	5.6
Tetramethylbenzidine	7.0	6.3
Benzidinesulphonic acid	7.4	4.8
Diamidostilbenedisulphonic acid	3.5	3.6
Dianisidine	6.9	5.7
Diamidonaphthalene	1.0	1.7

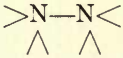
The following conclusions are drawn by Vignon from the results recorded in this table. Fixation is held to be due to chemical action depending on molecular grouping. The dyeing is not due to the benzene nucleus containing free nitrogen atoms, or two nitrogen atoms joined together to form azo-groups, since diphenyl, ammonia, hydroxylamine, and azobenzene are not absorbed. The diamines, with the exception of *o*.-phenylenediamine and the hydrazines are absorbed to a considerable extent, and the absorption appears to be independent of the degree of saturation of the azotised molecular groups.

It is argued from these results that the dyeing property seems to be due to the grouping

$$>\mathrm{N}-\mathrm{R}-\mathrm{N}< \quad \text{or} \quad >\mathrm{N}-\mathrm{N}<$$

that is to say to the hydrazine N atoms united directly, or indirectly by means of aromatic residues.

It is further argued that in the case of the direct colouring-matters the nitrogen atoms unite with the cellulose molecule and then become pentatonic.



$$>\underset{\wedge}{\mathrm{N}}-\underset{\wedge}{\mathrm{N}}<$$

The fact that benzidine and tetramethylene-benzidine are absorbed by cotton, whereas the methyl iodide compound of the latter in which the nitrogen atoms are already pentatonic is not taken up, also lends support to this theory.

The thermo-chemical investigations of Vignon are instructive (*Bull. Soc. Chim.* 1890, 3, 405 and *Compt. Rend.* 110, p. 909), and are held by that investigator to support a chemical theory. Dealing first with silk in the "raw" and "boiled off" state, the following results were obtained:

Reagents N/1 sols.	Raw Silk,		Boiled-off Silk,	
	Calc. for 100 grms.	Cal. for mol. wt. in grms.	Calc. for 100 grms.	Calc. for mol. wt.
Water	.10	3.5	.15	5.2
Pot. Hydrate	1.35	47.0	1.30	45.25
Sod. Hydrate	1.55	53.95	1.30	45.25
Ammonia	.65	22.65	.50	17.4
H_2SO_4	.95	33.10	.90	31.35
HCl	.95	33.10	.90	31.35
HNO_2	.90	31.35	.85	29.60
KCl	.20	6.95	.10	3.50
	6.65		6.00	

The above figures represent the heat-units evolved, the average temperature of the experiments being 12° C. The formula for gum silk was taken as $C_{141}H_{232}N_{48}O_{56}$, and that of the boiled off silk as the same.

The alkalies removed some of the silk gum. The total number of heat-units evolved was 6.0 in the case of ungummed silk, and 6.65 in the case of the raw silk.

The results obtained in the case of wool were different.

Reagent N/1 sol.	Heat-units per 100 grms.	Heat-uuits for $C_{88}H_{149}N_{27}O_{27}S_3$
KHO	1.16	24.50
NaHO	1.15	24.30
HCl	.95	20.05
H_2SO_4	.99	20.90

These experiments were made on unbleached woollen thread.

Turning to cotton it was noticed that the rise in temperature took seven or eight minutes to reach its maximum. The following results were obtained :

Reagents.	Cotton thread unbleached.		Cotton wool bleached.	
	per 100 grms.	$C_6H_{10}O_5$.	per 100 grms.	$C_6H_{10}O_5$.
KHO	.80	1.3	1.4	2.27
NaHO	.65	1.05	1.35	2.20
HCl	.40	.65	.40	.65
H_2SO_4	.38	.60	.36	.58

The effect of bleaching on the thermo-chemical reactions in the case of cotton is important. Vignon considers that the difference is due to the presence of oxycellulose in the latter.

These results would in themselves indicate that a chemical reaction may take place under the recorded conditions. It has, however, been shown (Göppelsroeder, *Centr. f. Text. Ind.*, No. 38) that both indigo and Turkey Red are attracted with greater avidity by oxycellulose and chlorocellulose, but there does not seem to be much evidence that chemical action can take place in the dyeing of these colours.

Furthermore (*Chem. Zeit.* 23, 1891), Vignon experimented with the object of increasing the activity of cellulose fibre by chemical means. Treatment with ammonia at 100°—200° C resulted in the fibre taking up nitrogen. The result in the calorimeter with this product indicated that the fibre was more basic. This treated fibre will attract large quantities of acid dyes giving dark shades.

The influence of this treatment seems to be very great, and the attraction for dyes is increased.

Experiments with stannic and metastannic acids also give important results when they are "dyed" with phenosafranine.

Stannic acid absorbed 63 per cent. of the dye in a standard solution.

Metastannic acid absorbed 0 per cent. of the dye in a standard solution. The more strongly acid oxide fixes the most colour.

Vignon sums up the results of his experiments (*Chem. Zeit.* 10, 1891), and considers that the following facts are in favour of a chemical theory.

(1) Thermo chemical reactions of fibres.

(2) Increased affinity shown by ammonia treated cotton.

(3) Action of the oxides of tin.

The chief arguments in favour of chemical action are summed up by v. Georgievics as follows:

(1) Magenta, methyl violet and chrysoidine are decomposed by silk and wool, hydrochloric acid remaining in solution.

(2) Rosaniline base is colourless. The salts are coloured. Wool is coloured when dyed from an ammoniacal solution of the base (Jaquemin).

(3) The red solution of amidoazobenzenesulphonic acid dyes a yellow shade. This is the colour of its salts.

(4) Picric acid and Naphthol Yellow are taken

up in quantities proportional to their molecular weights.

(5) The thermo-chemical reactions of the fibres.

It is pointed out, however, that the decomposition of the basic dyes is brought about also in the presence of porous inorganic materials, as the following figures will show. The presence of an animal fibre is not necessary.

Colouring-matter.	Amount taken.	Cl in same,	Colour left in sol,	Cl left in sol.
Magenta . .	.2045	.0166	.08	.0158
Methyl violet .	.2007	.0152	.09	.0152
Chrysoidine .	.2015	.0309	.122	.0265

It will be seen that the proportion of colour base taken up by the porous material is 53 per cent. against only 8 per cent, of the chlorine.

Glass beads will act in the same way, decomposing the hydrochloride of the base.* Wool takes up more hydrochloric acid at 45° than at 100° C, so does porcelain.

It is said that a rosaniline base can exist in two forms, and that the base is dark violet if precipitated in neutral solutions. The base, therefore, may exist in two forms: (1) As carbinol (colourless); (2) As ammonium base (coloured).

A colourless aqueous solution of the base does not, therefore, exist as Knecht states, and Jacque-

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* It has recently been stated that Jena glass will not act in this way, owing probably to its great insolubility.

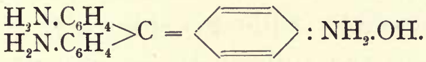
min's experiments may be explained as follows. The wool and silk absorb the base from the solution, and since the alkali is not taken up by the fibre the wool is coloured red.

There seems to be some doubt as to the existence of the coloured ammonium base. H. Weil considers that the colour is due to unchanged magenta in the precipitate.

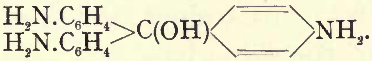
V. Baeyer (*Ber.* 1904; 2849) also doubts the existence of v. Georgievics' coloured ammonium base.

Hantzsch (*Ber.* 1900, 752), on the other hand, holds that the rosaniline bases are capable of existing.

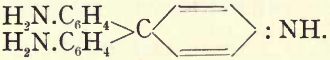
(1) True colour base:



(2) Pseudo ammonium base:



(3) Imide or anhydride base:



Further work on the absorption of dyes by inorganic substances has been undertaken by Gmelin and Rotheli (*Zeit. f. angew. Chem.* 1898, 482).

Glass beads were dyed for eleven weeks under identical circumstances with (1) Magenta; (2) Magenta and ammonia; (3) Rosaniline base. They were all dyed to the same shade.

Each lot was then washed with alcohol. The two last lots soon lost their colour. The first kept its colour for some time, and was even then not decolourised.

It is argued from these results that magenta may dye in two ways, the one chemical, and the other mechanical.

These results are held to confirm the existence of two states of one magenta base, and that the carbinol base is fairly stable, and requires strong acids to convert it into the ammonium base. The conversion of the one into the other in the presence of silk is explained by assuming that the silk acts as an acid.

Some experiments on the alkylation of magenta compounds also seemed to point to chemical action. A skein of silk dyed with magenta was allowed to stand in the cold in contact with methyl iodide in methyl alcohol. Side by side, and in the same mixture, were rosaniline base, rosaniline hydrochloride (magenta), rosaniline stearate, and the amido-stearate of the same base.

The only change noticed was the alkylation of the rosaniline base. This changed to a deep blue. The inference is that the magenta is present in the silk in a state corresponding to the hydrochloride, stearate, &c. In other words, it is combined with the silk. Unfortunately, it was not proved at the same time that the insoluble basic salts act in the same way as the base itself, and not as the normal hydrochloride. Until it is settled that the magenta is not present in this state on the silk, these results are inconclusive. At a temperature of 35°–40° C alkylation took place in all cases. They all turned dark blue.

The colour of amidoazobenzenesulphonic acid on the fibre is held by v. Georgievics to be yellow because the amount of dye present is not sufficient to dye it red.

Attempts have been made by Prudhomme (*Rev. Gen. des Mat. Col.* 1900, 4, 189) to replace the fibre by a liquid for experimental purposes, with the object of studying the results obtained under these conditions. Taking a solution not miscible with water, he dissolved salicylic acid or a weak base (acetanilide) in the same. A substance like phenylglycocoll may be added containing both basic and acid groups. "Dyeing" with basic colours, different shades to those of the solution were obtained in the "artificial fibre." They corresponded with those obtained on silk with the same dyes. Similar results were obtained with the sulphonated acid colours, using acetanilide as the "artificial fibre." That silk and wool behave like amyl alcohol containing the above substances is the conclusion drawn from these experiments.

The presence of salt-forming groups in the alkylated diazo direct dyes is said to be proved (Mayer and Schafer, *Ber.* 27, 3355), and this is put forward as a possible explanation of the absorption of these dyes by cotton.

The impurities present in the cotton fibre may influence its dyeing properties in some cases. Schunck suggested (*J.S.C.I.*, 815), that this should be tested by dyeing samples of the cotton after each of the following operations; treatment with carbon disulphide, alcohol, boiling water, hydrochloric acid, and then alkali.

The evidence in favour of the presence of carboxyl groups in the silk molecule is fairly satisfactory. Carboxyl compounds are formed when silk is decomposed by barium hydroxide (Schützenberger and Bourgeois), and by dilute sulphuric acid (Cramer), or alcoholic potash (Richardson).

The result of dyeing wool with both acid and basic dyes at the same time, seems to offer some support to the chemical theory. Weber shows that this may be done if a skein of wool be dyed with Scarlet R. After being carefully washed, it will take up magenta. The percentage of this second dye will also be the same as that taken up by a white skein. Furthermore, the lakes produced by the combination of acid, and basic dyes are soluble in alcohol, but this solvent will not remove these dyes from the fibres.

It has not yet been shown that a second acid dye will not enter a saturated fibre already dyed with a colour of this class, or that a basic dye will not adhere to a basic dyed fibre. This would necessarily follow if the second colour did not displace the original one. Further work is necessary before these points can be cleared up.

Weber's statement that the benzidine dyes are attracted both in the free state and as salts, is confirmed by Gmelin and Rotheli (*Zeit. f. angew. Chem.* 1898, 482). The barium salts of benzopurpurin 4B and benzoazurin 3G were prepared in as pure a state as possible. They both dyed cotton, and subsequent analysis proved that the dye was present on the fibre as the barium salt, and that no decomposition had taken place during the process of dyeing.

Owing to their reduced coefficients of diffusion they dyed very slowly. Correspondingly they did not bleed when once on the fibre.

A microscopical examination of fibres in sections gives the following results : Wool dyed with Crystal Violet or Malachite Green shows equal distribution of dye throughout the fibre.

Cotton dyed with the direct dyes shows in cross section that the dyes are more concentrated in the centre of the fibre.

Under the same conditions silk seems to be dyed equally throughout. A similar result was noticed by the writer with the primuline dyes in the case of silk.

Returning to the basic dyes, these authors prepared the salts of palmitic and stearic acids, and dyed silk with them. The fibre was then dissolved in hydrochloric acid, but no fatty acids could be traced in the solution.

They also record the fact that the benzidine salts of Naphthol Yellow S were decomposed on dyeing, the benzidine remaining in the solution.

This is, perhaps, the place to notice some experiments of Schunck and Marchlewski (*J.S.D. and C.* 1894, 95). The tinctorial effect of plant extracts is greatly increased by boiling with acids, and the conclusion arrived at is that the effect produced is due to the decomposition of the glucoside and rhamnosides of the colour-substances present in the extracts. It is, therefore, necessary to assume hydrolysis to explain the actions noticed in practice when glucosides are used in dyeing.

It has been assumed that chrome mordants split up the glucosides in dyeing, and fix their colour constituents only (Hummel and Liechti).

The authors find that in practice this assumption is correct. In dyeing cotton with datiscin, rutin and quercitrin the sugar is left in the solution. In the case of ruberythric acid the decomposition did not take place.

It will be seen from the facts recorded in the last two chapters, that the evidence brought forward to prove that the action of dyeing is a chemical one, is both voluminous, and diverse, in its nature, and that many of the facts which at first sight seem to support this hypothesis appear less definite on further examination.

One of the most striking examples of this is seen in the fact that such an inert substance as porcelain will split up the basic hydrochlorides, in much the same way as silk will do under similar conditions.

The base may be held by combination in the second case; but it is clear that the action may take place in the absence of any organic matter whatsoever, be it an amido-acid, or of any other constitution.

It is therefore a matter of difficulty to give to the recorded facts their true significance.

The fact that most of the work done on this subject is of a qualitative nature, whilst in many cases the reagents, and fibres, are in an unknown condition of purity, greatly increases the difficulty of the problem.

It is not possible therefore to do more than record the results obtained in many cases, and leave the future to sift out the grain, and carefully weigh it as evidence against the facts which seem to favour a wider theory of dyeing.

It would seem that generally speaking, certain facts indicate that dyeing *may* be due to chemical action; but it is an exceedingly difficult thing to prove from these that the action is really of this order.

Until the time comes when we are able to explain the actions which take place when colloids react in the presence of solvents, and definitely assign to these phenomena their true value, it will be difficult to establish a strictly chemical basis for the reactions which take place in dyeing; or even to prove that such action is a determining factor in the processes of dyeing, mordanting, and the formation of certain lakes.

CHAPTER X

PART PLAYED BY COLLOIDS IN DYEING AND LAKE FORMATION

It will have been gathered from the reactions shown by colloids in general, and from the fact that both dyes and fibres belong to this class, that the part played by these bodies in dyeing may be an important one.

It has even been suggested that the fixation of the dye-stuff on vegetable fibres is analogous to the act of diffusion through colloids. This idea was first put forward by Müller Jacobs (*Text. Colourist*, Oct. and Nov. 1884).

Some time before this Schumacher (*Physik der Pflanze*), experimenting with such typical colloids as starch, cellulose fibre, membranes, &c., noticed that there was not only an absorption of liquids, but also of the solids in solution. He noticed that :

(1) The relative absorption of solids is greater, the more dilute the solution.

(2) The absorption decreases as the temperature increases.

(3) Total exhaustion does not take place even in very dilute solutions.

These results are applied to the absorption phenomena of vegetable fibres, and an attempt made to explain the action of dyeing with these fibres, which, unlike the animal ones, do not so directly absorb ordinary acid and basic dyes, and therefore cannot be so readily brought into line with any so-called chemical theory.

This explanation of the action of dyeing therefore originated in an attempt to explain more particularly the specific action of vegetable fibres towards dye-stuffs.

To accept this theory we must allow that the action of dyeing is due to the separation of the sparingly soluble colloid dye from the diffusible crystalloid, or solvent, by the dialytic action of the membrane itself; which then becomes obstructed,

(1) by the formation of insoluble precipitates;

(2) by the gradual obstruction of the colloids in the interstices of the fibres.

In order to dissolve these sparingly soluble or non-permeable bodies, we must first dissolve them in crystalloids or easily permeable solvents.

Dr. Jacobs describes an interesting series of experiments with the artificial membranes obtained, when a concentrated and neutral solution of aluminium sulphate is introduced into a not too dilute solution of Turkey Red oil. Membranes are in this way formed round the drops; and the diffusion of substances through them can be easily observed. For instance, when alizarine is mixed with the outer solution the colour diffuses into and colours the cell walls, but there is a total absence of colour in the interior solution. These experiments were carried further, and alizarine and a neutral solution of alumina gave a red lake in the cell wall, but here again the interior remained colourless.

This investigator proposed the following classification of dyes in the place of Bancroft's scheme, which divide them into substantive and adjective colours:

(1) Such substances as easily pass through colloids or fibres.

(2) Such substances as pass with difficulty (colloids).

(3) Substances which will not pass at all.

These classes are not considered to be distinct but to merge into one another and overlap.

The object of dyeing is, therefore, to fix certain substances within the fibre in such a way that the fibre cannot be easily deprived of them by the action of solvents. The means by which this action may take place are considered to be

(1) By producing precipitates in the fibre.

(2) By complete separation of a sparingly soluble colloid from the diffusible crystalloid or solvent, by the dialytic action of the membrane itself.

The mordanting and dyeing actions are therefore considered by this investigator to be based on the action of two, or more, differently permeable bodies. It is claimed also that this action may even give rise to actual decomposition of certain chemical compounds.

The action of mordants in the fibre is a double one. It may either form precipitates with the dyed material, or else reduce the permeability of the fibre substance.

The reason why vegetable fibres do not dye easily is also explained by assuming that they are more easily permeable than the other fibres. This is perhaps not the generally recognised view of the case.

Similarly, mercerising or oxidation of the fibre does not act by reducing this action, but by increasing it in some cases.

The presence of albumin, casein, &c., on the fibre increases the colloidal nature of the fibre, and therefore the laws of dialysis will produce more powerful effects.

In this way Müller Jacobs attempts to explain the action of dyeing.

The effect of tannic acid in its mordanting action is to narrow the interstices of the fibre, and then combine with the dye to form a precipitate. The proof of this action is said to be demonstrated by the fact that in dyeing alizarine on an aluminium mordant the latter must be present in great excess. Fifteen times the alumina necessary to form the normal salt ($C_{14}H_6O_2.Al_2O_5$) must be present to give the best result.

The action of acids, tartar, &c., is said to prevent the superficial fixing of colours.

An attempt to extend this theory to the animal fibres is based on the fact that oiled cotton will dye red with rosaniline hydrochloride. It is considered that this is evidence that the dyeing of animal fibres is not a chemical action.

In this and in other ways this theory is supported. For instance, many organic colloids are hardly diffusible into animal fibres owing to their insoluble nature. The sulpho-acids of these substances being more soluble in water give better results. They can more readily penetrate the fibres. Alizarine carmine and sulph-indigotine are given as examples. They are both more soluble than alizarine and indigo, and therefore dye the fibres in a more satisfactory way.

On the other hand, these sulpho-acids may be too diffusible for vegetable fibres.

Assuming also that the dyes become more like precipitates, as their nature becomes more complicated, and as the amount of carbon they contain increases, it might be expected that the complex members of a group of colouring-matters would require to be present as sulpho-acids for dyeing purposes. This seems to be the case with the rosanilines.

The amido-benzenes are also quoted as an example.

(1) Amido-azobenzenes (Aniline Yellow) is sparingly fixed on cotton even as the sulpho-acid.

(2) Diamido-azobenzene (Chrysoidine) dyes cotton well.

(3) Triamido-azobenzene (Phenylene Brown) dyes well.

This action with the sulphonic acids is not a general one. For instance, the indulines are insoluble, and sulpho-acids form more or less readily, but these will not dye cotton. It is considered that they are, in this case, too diffusible.

The general conclusions arrived at were as follows. The permeability of a substance increases with rise in temperature, and fibres with narrow interstices require a higher temperature in dyeing. Wool would come into this class. It is also considered that when mordanted cotton is dyed at a low temperature, the relatively large interstices become smaller by deposition of the dye-stuff, and then a gradual rise in temperature is required to complete the dyeing operation.

If, on the other hand, the cotton is immersed initially in the boiling dye-bath, the colour will pass through these large interstices, and the material remain undyed. The mordant in this case is dehydrated, and the colour cannot be fixed.

From this point of view the case of the colourless sulphonic acids and their absorption is of interest. Is dehydrothiotoluidine sulphonic acid the only one in a highly colloidal state? This might be capable of direct proof. This theory has been roughly outlined. Further particulars will be found in the original papers.

There is direct evidence from the work of Picton and also from that of Krafft (*Ber.* 1899, 32, 1608), that high molecular dye-stuffs, such as the direct azo dyes, are colloids.

A series of experiments with Magenta, Methyl

Violet and Methylene Blue gave values by the ebullioscope in alcoholic solutions very near to the true molecular weights. In water, however, the colloidal state is taken up.

This result may be due to dissociation, and the less soluble nature of the base; or perhaps to association.

It is interesting to note also that tannic acid is said to be a very perfect colloid (Strutz and Hofmann), and to consider, as we have done elsewhere, the action of this acid.

In the case of wool and silk, Krafft considered that the fibre itself takes part in the interaction in dyeing; but that in the case of cotton the action is of a more indeterminate nature.

We may learn much concerning the properties of colloids in the hydrogel state, and their action, from a study of the phenomena which occur in the formation of coloured lakes, for pigments and printing purposes. This subject has been more or less exhaustively studied from the practical point of view by O. Weber. The results in detail may be studied in the original papers.

It is well known that basic dyes (hydrochlorides) will fix themselves on indifferent substances, such as starch, cellulose, alumina, china clay, &c. In this way pigments may be formed.

The dyes are, however, very loosely held, yielding readily to water. They are also very fugitive to light (Weber, *J.S.C.I.* 10, 896).

It is also noticed that these dyes do not give identical shades on these different media. This effect is also noticed in the case of dyeing on fibres, with this class of dyes. The shades obtained on cotton, wool, and silk, will often materially differ from one another, so that this action seems to be a general one. The student will at once realise the general nature of these dyeing operations.

It is interesting to note that tannic acid, which has been of great value in the dyeing of cotton with basic dyes, is not much used in the production of lakes. When, however, the manufacturers will trouble to prepare their basic lakes in this manner, they are well repaid. The fastest possible lakes are produced from these dyes in this way.

The fact that those lakes produced in indifferent substances, are so extremely fugitive under the action of light deserves attention. A comparison between their fastness on textile fibres, and on the indifferent substances, should be of interest.

It is noticed also that the attraction which these inert substances have for basic dyes is modified by the nature of the acids which enter into their constitution.

Roughly speaking, the amount of dye fixed is inversely proportional to the respective strengths of the acids, with which the bases are in combination. As a proof of this Weber gives the following results, which show the relative amounts of colour taken up by 100 parts of alumina. Under the standard condition of the tests 2 grams of alumina were suspended in 500 cc. of water.

Colour used.	Absorbed by 100 pts. Al_2O_3.
Bismark Brown G.	8.3
Acetate of Magenta	7.13
Methyl Violet B.	4.87
Brilliant Green	3.85
Magenta	3.53
Indazine M.	1.96
Methylene Blue B.	1.62
Thioflavine T.	1.43
Solid Green, Cryst.	1.21
Safranine G.G.S.	.83

There seems to be a good deal of evidence to prove that these dyes when present on inert substances are in the form of basic salts, varying in constitution between the normal salts, and the bases themselves.

That they are not present as simple colour bases is proved by the fact that the bases themselves are for the most part colourless. This fact is to be remembered in connection with the dyeing of these colours on fibres. These basic salts, unlike the normal ones, are very insoluble in water. For example, a "dissociation" lake may be produced on china clay by precipitating Benzaldehyde Green in the presence of Glauber's salt, or acetate of soda.

With this reduction in the "acidity" of these precipitated basic compounds, a corresponding loss in intensity of colour is noticed. The lakes produced in this way are partly decolourised, and an addition of tannic acid will develop the colour in some cases to the extent of fifty per cent.

If one of these basic lakes be washed with boiling water, only traces of colouring-matter go into solution, and the lakes ultimately become colourless. In the same way, tannic acid, by reducing the basicity of the colour salt, will bring the colour back to a great extent. This reaction is important and the action of solvents on basic dyes present in the fibre area cannot be correctly estimated by the altered colour-effect produced in this way.

It is known to every silk dyer, that washing with water will decrease the intensity of the shade in many cases, and a subsequent treatment with weak acid will bring the colour back. This subject should receive further attention. Light should be thrown on the state in which these dyes are present in the silk fibre. In the formation of lakes with tannic acid the action seems to be of an indefinite nature (O. N. Witt). The amount of tannic acid required to produce a true lake of a thoroughly saturated nature, as compared with the amount required to precipitate the basic dye perfectly from an aqueous solution, is indicated in the following table.

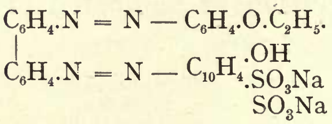
Colouring-matter.	T. A. actually absorbed.	T. A. required for mere precipitation.
Magenta	622	173
Methyl Violet	510	138
Solid Green	1324	456
Methylene Blue	620	198
Chrysoidine	322	194

Weber was unable to indicate the course taken by the interaction between the dye and tannic acid. It does not follow in the lines of chemical attraction, as indicated by the constitution of these dyes. The action seems rather to be on the lines of colloid precipitation, and may be regulated by the state of the precipitate. For instance, 100 parts of the magenta tannic acid compound will absorb 160 extra parts of tannic acid if present in excess, while 100 parts of the chrysoidine tannic acid compound will only absorb 60 extra parts of tannic acid under the same conditions.

The fact that the tannates of antimony, zinc, tin, lead, or iron will give better and faster lakes than tannic acid alone (Witt) is an interesting point.

Many organic acids form lakes (or insoluble compounds) with the basic dyes, and nearly all the aromatic acids act in this way. A similar result is also obtained with phosphoric acid, arsenious acid, or silicic acid when present as their alkaline salts.

The action of albumin on some dyes is of interest. For instance, Diamine Scarlet B



$$\begin{array}{l} C_6H_4.N = N - C_6H_4.O.C_2H_5. \\ | \\ C_6H_4.N = N - C_{10}H_4\begin{array}{l}.OH \\ .SO_3Na \\ SO_3Na\end{array} \end{array}$$

gives a very clear solution, and is not precipitated by dilute acids. If this be added to a solution of albumin a decided precipitate is obtained. It is, however, very difficult to filter, being of a slimy nature. To precipitate all the dye a large excess of albumin is necessary. If, however, the solution be heated to 80° C the albumin coagulates, and carries down with it the whole of the dye, in the form of brilliant scarlet flakes.

If this precipitate is boiled with water it will give up some of its colour to the solution. The lake is also slowly decomposed by soap solution at 50° C. The lake on drying gives a heavy solid, which shows little sign of swelling, or solution, in water, and soap solution at 80° C scarcely affects it.

Acetic acid may take the place of heat in precipitating the lake, but this acid will not precipitate either the dye, or the albumin by itself.

This action is not confined to direct dyes. Sulphonated basic dyes, azo dyes, and sulphonated nitro bodies act in the same way.

It would seem that for two substances of the above nature to "precipitate" one another, one of them must be in a state near to the point where actual precipitation, or coagulation, takes place. Gelatin, for instance, is incapable of this precipitating action, but albumin in a sensitive condition, at either 80° C or in the presence of cold acetic acid, will precipitate the dye.

The influence of the dye itself also helps, or retards, this action. Diamine Scarlet will precipitate albumin in the cold. Eosine, on the other hand, will only act in this way at a high temperature.

It is said that the shades obtained correspond exactly with those obtained on wool, or silk.

If the basic dye had combined with the albumin in the cold, a precipitate would probably have been formed, and this indicates, so far as it goes, that the action between the albumin and the basic dye is not of a chemical nature.

For some reason the fastness against light of these precipitated lakes varies with the nature of the precipitant. Albumin lakes are said to be four times as fast as the corresponding barium lakes, using the same dyes. The extremely fugitive nature of the basic dyes on a china clay basis has been already noticed.

This may be due to two causes:

(1) Difference in size of the dye aggregates.

(2) Difference in the way the dyes are held.

Arguing from the extraordinary sensitiveness of diazotised primuline, when produced in a colloid substance, the size of the aggregates may affect the action. The matter is one which demands attention, and a further study of this matter may lead to interesting results.

Surface-Concentration and Desolution Effects.—A modified theory on the above lines was recently brought forward (Dreaper, *J.S.C.I.* 1905, 233), to explain the general action of dyeing. It is founded on the work of Linder and Picton (*J.C.S.* 1892, 61, 148 and 1895, 63) and others, and attempts to explain the dyeing action on lines which are usually regarded as physical, although it is not denied that chemical action may supplement the actions, which lead to the general absorption of the dye by the fibre.

The work on pseudo-solution undertaken by

Linder and Picton has hardly received the notice it deserves by those interested in the subject of dyeing.

The dividing line between perfect solution, and suspension has broken down. The difference between the two states, is only one of aggregation; although it is not to be inferred from this, that any substance may, by successive stages, pass from the former to the latter state. This action is neither a reversible one in many cases, nor is it necessarily a complete one. In solutions of colloids the relationship between the solution, and the colloid (solute), is never complete, as in the case of a crystalloid. Solution stops short at some intermediate stage, and consequently, as has been explained elsewhere, the usual phenomenon of a lowered freezing-point of the solution is not in evidence to the same degree as in a perfect solution of a crystalloid. So far as appearance goes there is little difference between a colloid, and a crystalloid in dilute solutions; but an examination of the physical properties of the former in solution indicates that the differences in the solution state must be appreciable.

An interesting case of a colloid in a state of pseudo-solution is that of arsenious sulphide, which can be prepared in a state of such fine suspension, that the solution will pass easily through a porous pot without separation of the solid.

This is in itself a fact of general interest, but when we study the action of metallic salts on these pseudo-solutions the results at once become of interest to the dyer. In their action on these solutions, the different salts divide themselves into sharply defined groups, corresponding with their valency. As a general result the effect of the addition of these salts, is to degrade the state of the pseudo-solution. The aggregates become larger in size, and may even be precipitated. The salts of tervalent metals possess the highest coagulating power. Bivalent metals only act with one tenth of the effect and univalent metals with less than one five-hundredth part of the intensity in the first case. This difference in the power of precipitation, even extends to the same metal when the valency varies (*e.g.*, with iron). One molecule of aluminium chloride possesses the same coagulating power as 16.4 molecules of cadmium chloride, or 750 molecules of sulphuric acid.

When the coagulating action of salts on a solution of arsenious sulphide is studied in detail, unexpected results are obtained. As an example, when barium chloride is used as a coagulating medium, the barium is carried down, and the chlorine left in solution. Similar results are obtained with calcium chloride. The precipitated metal is retained, even after thorough washing with water, but another salt in solution will replace it.

This action is one of mass, and is not due to selective affinity, as it is reversible, and depends entirely on the proportion of the second salt in solution. For example, both calcium and cobalt salts will coagulate in this way, yet either will replace the other if present in sufficient quantity in the solution.

It will at once be seen that the influence of these experiments, on a strictly definite chemical theory of dyeing, is a disturbing one. A theory of mass action and the resulting affinity which is able to disturb such a system as that represented by barium chloride in solution might clearly take the place of a chemical theory of dyeing, and explain the experiments of Vignon and Knecht on the one hand, and of v. Georgievics on the other.

It will be seen, that we may equally expect a similar action with, say, rosaniline hydrochloride. In fact, with such an example before us, we can hardly set any limit to this action.

Extending their experiments to other substances Linder and Picton found that dye-stuffs such as Hofmann's Violet, Methyl Violet, and Magenta, gave interesting results.

The solutions of these dyes are so far perfect that the aggregates present are not sufficiently large to scatter light, as some of the arsenious sulphide solutions do, yet they were non-filterable. These results are altogether abnormal, from the point of view of the standards set up by these investigators for arsenious sulphide solutions, and we are clearly here face to face with an extension of the action in the case of these basic dyes.

Further experiments, however, showed that the porous material itself will absorb the dye if broken pieces of it were left in the dye solution. The authors did not carry these experiments to their logical conclusion, by identifying the action as similar in its nature to that of barium chloride, or they would have looked for a decomposition of the basic hydrochloride in the porous material. The cause of the decomposition of basic dye-stuffs in this porous material is uncertain. It is either due to a colloid state set up on the surface of the porous material, or else is due to "surface action."

Our knowledge of the actions which are associated with surfaces is incomplete, at the present time. It is possible to explain them in the following way. The material of which a porous pot is composed, by virtue of its liberal surface, and, as we know, slight solubility, will present to the solution a large surface in a colloidal state, and this by its action may decompose the basic hydrochloride, and precipitate the base.

It is just possible that capillary action may play a considerable part in the action. It must, however, not be lost sight of, that this action is directly connected with surface action. In fact, it is caused by it. The secret of capillary action being the greatly increased attraction at small distances (Hawkesbee).

The dissociation of the basic dye in solution, if it takes place, and its influence on such an action as the above, should make experiments on this subject important. Dyeing fibres and porcelain material, with dyes dissolved in mixtures of alcohol and water in varying proportions, should be undertaken, and their relative actions noticed.

The influence of the addition of sodium chloride, or other salts, on pseudo-solutions of arsenious sulphide is, by analogy, of great importance.

The solution becomes non-filterable, and therefore degraded in the scale of solubility. The action of such substances on dye-solutions is well known. The importance of this action is considered by the writer, to be not so much that caused by a decreased solubility of the dye in the solution, as the solid solution theory requires, but that the increase in the size of the aggregates and their degradation in the scale of solution, is the important condition; and that this is the cause of the modified result obtained in the presence of a suitable fibre.

Furthermore, the effect produced by filtration shows that the degradation of the arsenious sulphide solution is specific. The effect is as if all the aggregates present are increased in size.

From this and other considerations, the writer has put forward the hypothesis that in any system of a hydrosol, and to a modified extent in the case of a hydrogel, the size of the aggregates is determined by the two factors, the mutual attraction of the molecules and the solvent action of the solution. This latter factor may be the attraction of the solute molecules for those of the solution. When an equilibrium is actually set up between these two opposite forces, the aggregates will be of a definite size, and remain so until the system is modified by some secondary action, and the colloid either degraded in the scale of solubility, or the reverse.

It will be seen that the action of salts on a solution of a direct dye is capable of explanation. It has already been pointed out that the direct dyes do not give true solutions in water. That is to say, they give pseudo-solutions. The action of salts should give the same results in both cases, and there is no evidence at present that such is not the case.

The influence of different solvents on the molecular weights, or size of the aggregates, is undoubted. For instance, the following table shows the number of double molecules of nitrogen peroxide in different solvents (Walker).

Solvent.	Double mols. at 20°. Per cent.		Double mols. at 90° C. Per cent.
Acetic acid	97·7	...	95·4
Ethylene chloride	95·8	...	91·3
Chloroform	92·3	...	85·5
Carbon bisulphide	87·3	...	77·5
Silicon tetrachloride	84·3	...	77·4

It will therefore be seen that for some reason, probably owing to the relative attractions between the solvent molecules, and those of the solute, the state of aggregation varies greatly with different solvents. In the case quoted the state of aggregation is never very great, at least, as compared with that known to exist in the case of the so-called colloids, but it will sufficiently well indicate the action which takes place.

The influence of increased temperature may also be indicated in terms of the molecular state of the solution.

The increase in molecular weight in more concentrated solutions, is indicated also in the case of a solution of alcohol in benzene, and for this purpose the following table is quoted.

Concentration. Per cent.	Mol. weight (Alcohol = 46).
·494	50
2.29	82
3.48	100
8.8	159
14.6	209

This would also seem to indicate that association increases with molecular strength of solution.

Effect of concentrated solutions.—The increased effect produced in concentrated solutions of dyes is also explained by assuming that the size of aggregates is constant in any solution of this nature. From this point of view, the aggregates are larger rather than more numerous in the more concentrated solution.

So that we have alternate means of producing larger aggregates.

(1) By degrading the solution by means of the addition of salts.

(2) By increasing the concentration of the dye solution.

Both of these methods answer in practice, but as will be pointed out later on, the former is likely to be the more efficient, owing to the additional effect produced by "surface concentration," and, in practice, the saving in dye material is an important factor.

We know that molecular aggregation extends to the state we call solution, and this is a further proof that there is no dividing line between a colloid and a perfect solution.

It is therefore suggested that the aggregates are, within certain limits, constant in number rather than in size, as the strength of the solution alters.

With increased concentration, there comes a time when the aggregates are so large that their relations to the solvent assume a new phase. The point at which they occupy a space larger than the physical conditions of the liquid will allow may be a critical one. In crystalloids, which do not pass through the colloid state, but are controlled in their desolution by molecular forces which directly determine their ultimate solid state, this point is a sharp one, and gives rise to a separation of the salt, probably in the crystalline form.

With colloids, or substances which take a hydrated form, the course adopted is a different one, and between the pseudo-solution state, and that of the absolutely dry substance, there is no sharply defined dividing line; but merely a slow passage from one state to the other as determined by the relative proportion of water molecules present, although the actual point at which the hydrosol is coagulated, may be a critical one.

With decreased amount of solvent certain other phenomena come into more active play, and an automatic separation of the colloid material may actually take place from these secondary causes.

Closely connected with the subject of the constant size of the aggregates in a hydrosol is the mechanism by which this can be determined; here we must assume molecular migration (Dreaper, *J.S.D. and C.* 1905).

This is not an impossible condition. Actual atomic migration has already been assumed by Poisson, and this being so, it is held by the writer that the forces which are called molecular are similar in their nature to those which are called atomic. Such a migration is a necessary adjunct to any theory of association between a liquid, and a solute.

There is also a certain amount of evidence that these changes do occur in a solution, and that they can be actually observed, as the case of very viscous solutions, like those of nitrocellulose in organic solvents. The observed fact of the " ripening " of such solutions is held to be due to an action of this kind. Several months elapse in some cases before the ultimate state of equilibrium between the solvent and solute is reached.

If we assume this action, it is also possible to explain the slow dialysis of colloids through membranes, which is theoretically possible, and has been observed in the case of nitrocellulose by de Mosenthal (*J.S.C.I.* 1904, 292). If we assume the migration of individual molecules from one aggregate to another, it is possible for these aggregates to pass gradually through a membrane, by some such secondary action, although they themselves are incapable of passing directly from one side to the other.

In the action of dyeing there is a constant play of altered conditions due to temperature, alteration in concentration, &c., and consequently, a constant variation in size of the aggregates, which in itself will entail this roving state of the individual molecules.

It has also been established by Linder and Picton (*ibid.*) that a 4 per cent. solution of arsenious sulphide is non-filterable under ordinary conditions. This would indicate that the aggregates are larger in size, and support the above conceptions.

Support is seemingly given to these views by the observed action of the following complicated and obscure cases in general dyeing.

If a logwood iron lake be dissolved in a dilute solution of oxalic acid, it will, as is well known, dye silk and other fibres a deep black colour. In its original state the lake is insoluble. The particles or aggregates have in its preparation been so degraded in the scale of solution, that they are no longer within the limits of dyeing requirements. By the gradual addition of oxalic acid to a suspension of this lake in water, the size of the aggregates is in some way gradually reduced, passing by stages of colour from black through brown to an almost golden colour, as the proportion of oxalic acid is increased.

Assuming that the lake in its more soluble state passes through a corresponding state of pseudo-solution, we arrive at the following conclusions. The aggregates in this state come into close enough relation with the fibre substance for de-solution to take place from whatever cause, be it surface attraction, or concentration, or mass attraction at short distance. At any rate, the solution state, whatever it be, is disturbed by the presence of the fibre, and the solution state is degraded with the precipitation of the lake in the substance of the fibre. Alizarine lakes in the "one bath" method of dyeing also seem to act in the same way.

From the above theoretical considerations, it would also be expected that, if the molecular proportion of oxalic acid be increased, a point will ultimately arrive when from one cause or the other a decreased de-solution effect will be produced. This actually occurs in practice.

It would follow also that at this stage a further addition of lake, or a reduction in the amount of free acid, would increase the size of the dye aggregates, and cause a reversal of the action. This is also actually observed.

The colour-effect in the solution is also completely reversible, and runs parallel with the dyeing results.

Under certain conditions silk and wool fibres are capable of attracting from aqueous suspension certain insoluble amines (Pokorng, *Bull. Soc. Ind. Mulh.* 1893, 282), if they are in a state of fine division.

Naphthylamine, if dissolved in a small quantity of alcohol, and poured into water, will impregnate wool in twelve hours in the cold.

The fixing is said to be entirely mechanical, and the amine is easily removed by water.

These results have been confirmed by P. Werner (*ibid.*), and further experiments show that the result is directly influenced by the proportion of alcohol to water. As the alcohol increases from 5 to 30 per cent. the absorption increases. Beyond this a reverse action sets in on similar lines to that of the logwood-iron-lake solution, and with essentially different substances he obtained the same effect. As the alcohol increases so does the solubility. Up to a certain point this leads to increased dyeing effect. Beyond this, the action of the alcohol on the hydrated fibre state, and the decreased size of the aggregates, tell against absorption.

The action of a more efficient solvent (alcohol) on dyes in fibres is to reduce the size of the aggregates. Under these circumstances the dye, or part of it, may leave the fibre. This is noticed in many cases, and it tends to indicate that such dyeing actions in mixed solvents is more due to the solution state than to the fibre state, but a great deal more work will have to be done on this subject before it will be possible to apportion to each action its qualifying effect.

The action played by water is still obscure. It may be that it is indicated by the statement made by Pokorng, that while pure alcohol will not extract some dyes from the fibre, yet 95 per cent.

alcohol will do so. (*See* page 167.) This may indicate that the pure alcohol cannot enter the fibre, and that a semi-hydrated state is necessary before the colour can be extracted. Otherwise some more complicated and unknown action is involved.

Experimental evidence as to the relative solubility of the dyes in mixtures of alcohol and water, both in the presence, and absence, of a fibre substance are wanting. Also there is no evidence available to show whether the fibre absorbs more water than alcohol from mixtures of the same. Both these points will be made the subject of investigation.

It is possible that the dye aggregates are associated with solvent molecules, in fact, are doubly complex in this way. The same applies to the fibre. If we have molecular migration, the aggregates may even join up loosely with the fibre aggregates, and in this way the fibre and dye be held together by some such secondary attraction.

The third case given as evidence in favour of these theoretical conclusions is taken from some work done by Binz and Bing (*Zeit. f. angew. Chem.* 25, 1902), on the relative action of salts on the dyeing of wool with indigo, in cases where the alkalinity of the bath varies.

The addition of neutral salts, such as Glauber's salt, sodium chloride, &c., does not intensify the shade so long as the alkali is only present in sufficient quantity to dissolve the indigo white. In the presence of excess of alkali, the addition of neutral salts has an intensifying action, and as a result, darker shades are produced on the fibre. The presence of 1·8 per cent. NaCl, for instance, doubles the amount of indigo absorbed by the fibre.

In the presence of a large excess of alkali, this increased dyeing effect on the addition of salts is not nearly so pronounced.

It is not difficult to see that here, also, we may find an explanation of the effect of these substances in the presence of excess of alkali; when the state of solution is of a more perfect nature, it might be expected that the action of salts would be correspondingly reduced, and this would naturally effect the dyeing result. It must always be remembered that the fibre state may also be profoundly modified by the presence of these substances in solution.

So that, as is pointed out, by a careful adjustment of the excess of alkali to that of the salt, a satisfactory state of the fibre, or one of maximum absorption, may be obtained, and the best dyeing effect be produced.

This is the condition which would naturally be aimed at by the practical dyer, from the point of view of economy.

It is of great importance to note that the alkali is evidently not fixed on the fibre in any way, and it is only necessary to take account of the fixation of the indigo white. V. Georgievics (*Der Indigo*, 1892, 55) has shown that it is only the latter which is fixed, the alkali remaining in the solution. The results obtained by Kœchlin as a result of a study of the absorptive power of cotton for tannic acid are of interest from this point of view. It is known that tannic acid gives pseudo-solutions.

Experimenting with different strengths of solution abnormal results were obtained.

The point of maximum absorption seemed to coincide with a concentration of .2 per cent. Beyond this reversal seemed to set in, for a cotton saturated in a .5 per cent. solution still absorbed tannic acid in a .2 per cent. solution. The state of aggregation, or else the mutual attraction of the tannic acid for the cotton fibre, is altered subsequently in a .02 per cent. solution, for in this the cotton just begins to lose tannic acid.

If figures could be obtained showing the relative action of cotton and mercerised cotton with regard to this reversal, the results would be of interest. In some such way as this it might be possible to indicate whether the action was due to the fact that the latter is in a more highly colloidal state, or whether the additional hydroxyl groups play a part in the action. A further study of this subject is contemplated.

It has already been noticed that the addition of acetic acid to the tannic acid solution greatly increases the proportion of the latter acid absorbed by the fibre. Apart from the value of this observation from the practical point of view, its possible influence on our knowledge of dyeing is obvious. The action is as difficult to explain in this case as in the case of silk or wool dyeing with sulphonic acids, or carboxyl dyes in the presence of stronger acids.

Surface concentration also, as the writer has pointed out, must play an important part in any theory of dyeing.

If the action of dyeing were purely chemical in its nature, this concentrating effect would have an important bearing on the *rate* of dyeing, but from the point of view of pseudo-solution it occupies a still more important position.

Assuming that dyeing is an action which is independent of any actual attraction between the fibre substance and the dye, it is very difficult to see how the fibre can attract the dye, or hold it.

It is this difficulty which made Cross and Bevan (*J.S.C.I.* 13. 354) accuse O. Weber of assuming a one-sided penetrability for the dye substance. That is to say, that the dye would diffuse into the fibre, but would not diffuse out again. If, however, one realises the possibility of this concentrating action at surfaces, the matter at once assumes a different aspect.

J. J. Thomson (*App. of Dynamics to Phys. and Chem.*, p. 251) pointed out that the most stable arrangement of any solution will be accompanied by minimal surface energy. The result of this action is distinctly seen in practice. There is a tendency with most salts to concentrate at surfaces, and for a similar reason, and to a correspondingly greater extent, in capillary tubes.

For instance, in the case of graphite or meerschaum, this concentration in the case of potassium sulphate is nearly 25 per cent.

It will be seen that the influence of this action in dyeing may be a profound one, for with the additional concentration of the pseudo-solution of the dye we shall have a rearrangement of the aggregates. The size of these will correspondingly increase within the capillary spaces of the fibre substance owing to this action.

The rate of diffusion will correspondingly decrease, and we shall arrive at a state where the osmotic action is greatly in excess of the exosmotic one. This can produce but one effect, viz., a concentration of the dye substance in the fibre area, and a state of "one-sided penetrability" is arrived at. When it is also recognised that the salts will also concentrate about and in the fibre area, it is easy to realise the possible result of this general action.

The effect of the concentration of the assistant and its influence on the state of aggregation may, it is held, be seen in the dyeing of silk with ordinary acid colours. If the dyed silk be introduced into water, some of the dye is readily removed. With the decrease in the concentration of the acid the aggregates may decrease in size, and be partly removed, or tend to re-enter the dye solution. This action is, therefore, a reversible one.

As a result, therefore, of this concentration effect, it is obvious that the dye may be degraded in the scale of solubility; that it may actually become insoluble.

In the case of dyeing with logwood lake by the "one bath" method, the fact that the colour of the silk fibre is not black, but dark brown, until the skein is finally washed in water, indicates that the dye state is one of degradation, rather than complete dissociation from the solution state during the time of dyeing.

In this case it is probable that the concentration of oxalic acid in the fibre area is small as compared with that of the dye-stuff. If this were found not to be the case it might indicate that some secondary attraction between the dye and fibre substances comes into play, and to that extent accounts for the displacement of the equilibrium of the dye solution within the fibre area.

The intensity of this surface concentration varies with different acids and salts. An elaborate series of experiments was conducted by Gore on this subject (*Birmingham Nat. Hist. and Phil. Soc. IX.* 1, 1893). The effect is directly dependent on the area of the surface. For instance, if a dilute solution of acetic acid be filtered through fine white sand, nothing but pure water will percolate through, the whole of the acetic acid being kept back by this action.

The following results chosen at random from a very full list in the original paper will illustrate the relative action of substances. Ten per cent. solutions were used in each case.

HCl	lost	2.88	per cent.	Tartaric acid	lost	1.42	per cent.
HI	„	1.0	„	Citric acid	„	nil	„
HNO_3	„	2.5	„	$CaCl_2$	„	3.1	„
$HClO_4$	„	4.4	„	NaCl	„	2.77	„

We have therefore, a physical reason for the concentration of substances in solution at surfaces, and the influence of this action cannot be neglected.

It will be seen that this is still more evident when it is noticed that this tendency to concentrate is stronger in the case of substances, in a state of pseudo-solution, than with salts which are more soluble.

In the case of substances of high molecular weight these surface concentrations may be so intensified by mechanical movement that the substances may heap up and form visible films of solid, or very viscous matter (Ramsden, *Proc. Roy. Soc.* 72, 156).

The size of the aggregates undoubtedly affects the general result. For instance, Gore found that the following substances gave positive, or negative surface attraction results, as indicated. It will be seen that substances in suspension give abnormal results.

Picric acid in solution	No result
„ in suspension	Result
Salicylic acid in solution	No result
„ in suspension	Result
Methyl orange	„
Orange G.	„

It may be that the molecules of soluble substances like, say, sodium chloride "salt out" dyes by means of the greater attraction between the solution and solute molecules in the case of more perfect solutions. In the case where these colloid substances are separated by the above mechanical means, they are not always resoluble in the solution. They are sometimes even insoluble. The action of aggregation is non-reversible under these conditions.

These separated films vary greatly in their physical properties. They may be membranes, membrano-fibrous, or fibrous as the case may be; or they may even consist of particles lying side by side.

The special surface viscosity which accompanies these separations, and which is indicated by a resistance to "shear," develops at very different rates.

These concentrations also occur at the intersurfaces of two solutions, and give rise to distinct surface tension phenomena at the junction of aqueous colloid solutions of different concentrations (Quincke, *Drude's Ann.* 10, 478).

In this action, coupled with the above laws of aggregation, and possibly, molecular migration, we have an explanation which will satisfy the dyeing conditions in a great many cases such as the "one bath" method, indigo and "sulphide" dyeing, the dyeing of direct colours on cotton, &c., without bringing in any complication due to chemical action. Dr. W. H. Perkin, senr., has pointed out (*J.S.C.I.* 1905, p. 235), that the surface character of silk, wool and cotton respectively can be shown to produce different results under the following conditions. A skein of cotton was worked for some time in an emulsion of olive oil and carbonate of potash, such as was used by Turkey-red dyers. On wringing it out afterwards, nothing but pure water left the skein; the cotton was practically free from oil.

On repeating this experiment with a silk skein the water was still nearly pure, but the silk retained a large amount of oil.

By substituting a wool skein for silk, and after rinsing the skein in water, the oil ran from the wool in quantity on wringing.

These experiments are of interest. The oil particles, or aggregates are of course much larger than in any case of pseudo-solution met with in dyeing, but the results produced show the very different nature of the absorption of such substances by these three typical fibres, and also indicate that the absorption which may, in this case, be taken to be of a physical nature, is very pronounced.

Dr. Perkin states also that the behaviour of these different fibres in relation to the oil corresponds closely to their dyeing power. This would not, however, seem to be a universal rule, especially with the direct colours, yet the phenomena recorded are certainly suggestive in their nature.

Some experiments of Chabrié (*Comptes Rend.* 115, 57) roughly indicate the limit at which it might be expected that concentration might take place in the fibre area. Experimenting with capillary tubes of a diameter of .07 mm., interesting results were obtained; on passing a solution of albumin slowly through such a tube a separation takes place, and only pure water passes through. The albumin is concentrated in the tube to such an extent that ultimately all flow is stopped. This would, in a case of dyeing, indicate the ultimate absorption point, or the dyeing limit, and the size of the inter-spaces in different fibres, and of the same fibre in different states of hydration, would of course greatly modify the action. The influence of this action is, therefore, evident, and will have a definite bearing on the best condition of the fibre substance for dyeing purposes, the object being to bring the greatest possible number of fibre molecules in contact with the dye aggregates without ultimate damage to the fibre itself by disintegration. A good example of this action is seen in the increased action of dyes on powdered wool under standard conditions.

In the cotton fibre, when the cellulose which has once been dried is not easily rehydrated, the aid of hydrating substances is necessary to obtain the best effect. Mercerising increases the power of the fibre in this direction. The mass action of a fibre will depend on its original construction modified by its capability of entering the hydrogel condition in the presence of water.

Extended treatment with water itself will, to a certain extent, take the place of the action of reagents in inducing this state. Continued boiling in water will induce this state in the cotton fibre, so that its attraction for certain dyes is materially increased (Hübner and Pope).

The bleeding of direct dyes on cotton indicates that the dye is loosely held, in fact, very much in the way it might be expected if the dye were precipitated, or held by de-solution, and subject to re-solution, either by molecular migration, or otherwise.

The experiments on the influence of temperature on the ultimate dye state of the fibre made by Brown indicate some such action as the above.

When the solubility of a dye increases with temperature, we may assume that, in the case of the direct dyes, which give pseudo-solutions (Schultz), the aggregates are correspondingly smaller at higher temperatures. Keeping this in mind, let us examine the results obtained with Kalle's Direct Yellow G. The amount of dye absorbed by silk, wool, or cotton increases up to 80° C. Beyond this point the curves for silk and cotton turn one way, and that for wool the other.

In the case of a fibre which gives increased absorption beyond this point, we must either have a more or less sudden change in the fibre state, or else the decrease in the size of the dye aggregates will allow of their more rapid diffusion into the fibre area.

In the case where a decreased absorption is recorded, the increase in dye absorption may be due to the aggregates becoming too small to be degraded in the fibre substance under the altered conditions. Such a case, where the absorption of a colour by silk and wool becomes greater in the one case, and decreases in the other, does not support a theory of dyeing which assumes a common cause of attraction (tyrosine) in these two fibres. The action may be complicated by changes in the fibre state, and it is necessary to consider the possibility of dissociation effects.

The writer has for some time sought an explanation of the abnormal fastness of Night Blue on silk fibres against the action of boiling soap solution, in light shades. In darker colours the fastness is not anything like so pronounced. Up to a certain shade the dye will withstand a treatment extending over half an hour. It would seem that here we have a case of dyeing, where the dye is held in two ways. The first portion is either in a very degraded state of solution, or else it is held by direct attraction or affinity.

This may be one of the cases in which dyeing is in one stage a process of chemical action. Taking everything into account, the writer suggests that the natural order of the phenomena which take place in dyeing is something of the following nature, depending on the factors :

(1) A solution state of the dye, within certain limits of aggregation, determined by the laws of size.

(2) A fibre state corresponding to this state of aggregation, and of a permeable nature.

(3) Effective localisation of the dye within the fibre area, due to surface concentration phenomena.

(4) Localisation of any salts, acids, &c., within the fibre area.

(5) The indirect entrance of the dye aggregate by molecular migration, with subsequent reformation of an even more complex nature within the fibre area, under conditions mentioned under (4).

(6) De-solution, due to secondary attraction between the fibre substance and the dye, or by reduced surface energy phenomena, or concentration effects.

(7) In some cases, primary or chemical action may play some part at this stage. This may, even in some cases, take the place of de-solution phenomena.

(8) In the case of basic dyes, dissociation effects may lead to the isolation of very basic salts in a state of high aggregation within the fibre area.

We have seen that barium chloride and other salts undergo decomposition in the presence of colloids, like arsenious sulphide. It is, therefore, not to be wondered at if actual decomposition of the basic hydrochlorides takes place within the fibre area. It is known that these dyes suffer decomposition of a partial nature, at any rate, by capillary action. It is also well known that the basic dyes become very insoluble when, by losing part of their hydrochloric acid, they become basic salts.

It is not difficult to indicate a state of affairs which would offer a satisfactory explanation of the fixing of these dyes in animal fibres, or degraded hydrogels, or even in the pores of such a comparatively inert substance as porcelain, or china clay.

It is difficult to imagine that the action of dyeing is a strictly chemical one. For instance, it is noticed that in mordanting cotton with tannic acid the best results are obtained by immersing the cotton in the boiling solution and allowing it to cool. The mordanting takes place at the lower temperature. The solution of tannic acid will be of a more perfect nature at higher temperatures, and therefore the aggregates will be correspondingly smaller. They will increase in size as the solution cools, and therefore become more readily fixed, especially if they re-form within the fibre area. This action is recorded by Brown (*J.S.D. and C.* 1901, p. 94), and is an interesting one, which is comparable in many ways to the reduced dyeing effect noticed in certain cases, at temperatures above 80° C.

The solvent action of alcohol, or benzene, on dyes which are already fixed on the fibre is an indication, perhaps, that these dyes are chiefly held by de-solution rather than by any process of primary, or chemical attraction.

In the presence of a solvent of higher power the aggregates are correspondingly smaller. A new system is set up, and the dye, or part of it, leaves the fibre. There is no question here of solid solution, but simply that of solution following de-solution.

The direct fixation of the dye may be due therefore to three causes :

(1) De-solution, including dissociation effects.

(2) Pseudo or secondary action.

(3) Primary or chemical action.

These three phenomena may overlap each other, there being no strict, or hard and fast division between them. It is held that there is evidence to indicate, that all substances during precipitation pass through the pseudo solution state.

An equilibrium between the relative attraction of the solution and solute molecules, on the one hand, and the molecular attraction of the solute molecules for each other will be established in any system.

In the case of very insoluble compounds the solution attraction is unable to break down the aggregates of the solute beyond a certain point.

In some cases, and by certain means, an abnormal state of aggregation may be induced in the case of these very insoluble substances, and we then arrive at a condition which, as in the case of some metals, is regarded as the colloid state. Analogy would suggest that this state is equivalent to the state of supersaturation in the case of a crystalloid, or a gas.

At this point in the case of a dye which is in a state of pseudo-solution, the only change which will take place will be due to molecular migration owing to local influences; or to the tendency to set up an ultimate state of equilibrium over the whole system.

Such is the de-solution theory advanced to explain the action of dyeing. The chief objection to it is, perhaps, that this action will be of too irregular a nature to explain the definite results obtained in some cases, which indicate that the ratio of absorption of certain dyes is in direct relation to the combining weights of the dyes absorbed.

It has, however, been recently shown (*see* p. 121) that the salts of calcium, strontium, barium and potassium are precipitated by colloids in the ratio of their chemical equivalents (J. Billitzer, *Zeit. Phys. Chem.* 1903, 45, 307).

The phenomena which present themselves in the presence of pseudo-solutions are sufficiently well marked to demand attention.

The conditions of surface concentration have been observed, and studied from a mathematical point of view; the experimental results recorded are beyond dispute.

The fact that de-solution may take place in the presence of a liberal surface has also been observed in the case of pseudo-solutions.

The action of precipitating agents on colloids is a definite one, as shown by the replacement of one metal by another, under the laws of mass action, as recorded by Linder and Picton, and the additional statement made by Billitzer, that the different metals are originally precipitated in the ratio of their chemical equivalents, when they are carried down by the degraded colloids. These precipitating actions are clearly definite, although they may not be strictly chemical in their nature.

This phenomenon of de-solution is, it is held, seen in the remarkable result obtained by Hallett on dissolving the colour off dyed yarn.

When dark shades of indigo were stripped in this way, the dye extracted by the solvent was also thrown out in the insoluble form as a precipitate. So that we have here a system where the one-bath method of dyeing may be seen reversed. Starting with the dye already fixed on the fibre, the conditions of dyeing may, from this point of view, be so far realised, that a condition of equilibrium may be established in which the indigo may be present on the fibre, in solution, and in the insoluble state as an actual precipitate.

The suggestion I have made, that an arsenious sulphide solution may be regarded as equivalent to an "artificial fibre substance," and that if we can have such an action with barium chloride, a similar action with a basic hydrochloride, or even a sulphuric acid salt is quite possible, has recently received confirmation (*see* p. 278). W. Biltz (*Chem. Centr.* 19052, 524) has shown that if the ordinary dyeing process be represented by the formula

$$\frac{Cn \text{ fibre}}{C \text{ dye liquor}} = K,$$

where C fibre is the concentration of dye-stuff in the dyed fibre, C dye liquor is that in the dye-bath, and the index n is greater than 1 (it is frequently found to be a whole number), then working with inorganic colloids and a suitable dye-stuff, there is no essential difference between the dyeing properties of coloured inorganic colloidal substances and organic dye-stuffs.

The comparative experiments were conducted with benzopurpurin on the one hand, and molybdenum blue, and vanadium pentoxide on the other.

In both cases the composition of the coloured fibre after dyeing, at a given temperature, depends on the conditions of the dyeing process, the concentration of the dye-stuff, and the nature of the salts added to the dye-bath.

Furthermore, with the substitution of the hydrogel of alumina for the organic fibre the same relations hold.

In the same way some experiments made by W. Biltz and P. Behre (*ibid.*) with dialysed solutions of Immedial sulphur dye-stuffs, which were free from alkaline sulphides, showed that these dyes were "coagulated" (or salted out) by electrolytes, and that the coagulating power of these substances increased with the valency of the cathion. This same effect, it will be remembered, is noticed in the coagulating experiments with arsenious sulphide solutions.

Again, in the case of these dyes similar absorption results were obtained when the hydrogels of alumina, zirconium dioxide, ferric oxide, and stannic oxide were substituted for textile fibres.

In this way the experimental results have shown that in the cases under consideration there seems to be a direct relation between the dyeing of the fibre, and that of inorganic hydrogels.

It is interesting to note that in the original work on the subject of the absorption of inorganic colloids by fibres (Biltz, *Chem. Centr.* 1904, I, 1039), the absorption is also increased by the addition of salt to the solution.

The general conclusions arrived at were that, by comparison, the solutions of the organic dyestuffs were subject to more complete exhaustion than those of the inorganic colloids, and that the shades produced are faster against washing, and rubbing. The addition of electrolytes to the solution led to more complete absorption in both cases. Increasing the temperature of the dye-bath also has the same general effect.

Weighted silk had an increased affinity for inorganic and organic colloids. The absorption was retarded by the presence of "protective colloids" in both cases.

A direct comparison between the dyeing action of molybdenum blue, vanadium pentoxide, ruthenium oxychloride, and silver, with benzopurpurin also indicated that they were of the same order when dyed on silk and cotton. The concentration, condition, and additions to the dye liquor affected the results (*Ber.* 1905, 2963).

The hydrogel alumina absorbed methylene blue, colloidal silver, and benzopurpurin; the fibre being replaced by this inorganic hydrogel without the absorption effect being altered.

In the case of the sulphur dyes colloidal solutions were prepared by dialysing solutions for ten to fourteen days. Cotton, aluminium hydrate, ferric hydrate, and oxide of tin, absorbed the dyes from these solutions (*Ber.* 1905, 2973).

Certain absorption results may take place with inorganic colloids, which have been long recognised in the preparation of lakes. The absorption seems to be of the same order as that which occurs in the dyeing of silk, or cotton with certain colours.

If the inorganic colloids are in the hydrosol state they may be absorbed by fibres or inorganic colloids. They may even be carried down by barium sulphate.

If the inorganic colloids are in the hydrogel state, they may absorb dyes in the same way as fibres.

Quite recently Linder and Picton, returning to this subject (*Trans. Chem. Soc.* 1905, 1930), show that ferric hydroxide is coagulated by a solution of Soluble Blue, $C_{38}H_{28}N_3(SO_3Na)_3$, or Nicholson's blue ($C_{37}H_{28}N_3.SO_3Na$) in the same way as it is by ammonium sulphate.

At a certain critical point a red coagulum separates which contains all the iron and the sulphonic acid, an equivalent amount of sodium chloride remaining in solution.

After extraction with alcohol a red precipitate remains, which is decomposed by dilute sulphuric acid, or salt solution. The hydroxy-dye-sulphonate is decomposed. The solution takes a deep blue colour.

With Methyl Violet, $C_{19}H_{12}(CH_3)_5N_3.HCl$, no coagulation takes place. Chlorides only coagulate ferric hydroxide in highly concentrated solutions.

With arsenious sulphide the order is reversed.

With Methyl Violet a hydrosulphide derivative is precipitated and hydrochloric acid remains in solution. Aniline Blue has no such power, but sodium salts only coagulate arsenious sulphide in highly concentrated solutions. Hofmann's Violet or Magenta acts in the same way.

These dye salts continue to take up the dye with avidity to an extent equal to four or five times the amount required to coagulate the hydroxide.

No decomposition takes place here; the dye is absorbed as a whole, not as a sulphonic acid.

Similar results were obtained with Methyl Violet and arsenious sulphide. These absorption results are confined to the class of dye originally taken up. The action here is therefore of a different nature from that by which basic dyes are held by a direct dye already present in a fibre.

It will be remembered that similar absorption results were obtained with tannic acid lakes.

The evidence here is, therefore, that the original action by which the two *hydrosols* are coagulated is of a chemical nature. This practically exhausts itself before the colour absorption stage commences; and this is of a physical rather than of a chemical character, in the case of the mutual attraction between the dye and the coagulum. These results led Linder and Picton to support the writer's desolution theory rather than Witt's hypothesis of solid solution. They further consider that the action itself is of an electrical character depending on the properties of the reacting units, by reason of which two oppositely charged hydrosols in strong aqueous solution seem to be mutual coagulants.

The fibre substance is of course already present in the insoluble state, and when in a hydrated condition may possibly be taken as equivalent to the coagula of the above experiments.

It must not be taken for granted in the present state of our knowledge that the dyes are always precipitated in the fibre by direct attraction. To do this it would be necessary to ignore the phenomena of surface concentration, which is particularly marked in the case of pseudo-solutions. This may, of course, be an electrical phenomenon. It will be realised that the influence of these general actions in the case of colloids cannot fail to be of value to the dyer in the art of dyeing and printing. These reactions also explain much that is obscure in the formation of lakes within the fibres, as in the case of alizarine colours; or in their direct production for industrial purposes.

They may equally modify our ideas on tanning, and the manufacture of leather.

CHAPTER XI

THE ACTION OF LIGHT ON DYEING OPERATIONS, AND DYED FABRICS

THERE seems to be evidence that the presence of light may materially alter the dyeing results obtained in some cases. The action of light in causing the fading of dyes present on the fibres is also a very important one to the dyer.

The action of light on organic compounds in general is but little understood. Our knowledge of this subject is incomplete, but it is already clear that the further study of it will bring forward many interesting facts for the consideration of the dyer. The list of substances which may be altered by the direct action of light under certain conditions is an extensive one. This has long been known to those specially interested in this subject from a light recording, or photographic point of view.

The action of light has been divided into two classes, viz., Photo-chemical and Photo-physical.

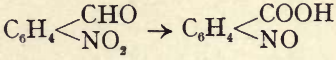
The division is perhaps an arbitrary one, but in the first case it is assumed that a direct action takes place which involves re-arrangement in the molecule itself. In the second case, the action is said to be equivalent to, say, the polymerisation of formaldehyde.

Marckwald, in attempting to explain the action which takes place in cases where the alteration is followed by a reverse action in the dark, considers that the actions which take place in this case are not to be explained by either of these causes. To the above classes he therefore adds a third, and suggests that this special reversible action shall be termed photo-tropical. Examples of this are seen when light acts as quinoquinoline, or tetrachlor-β-ketonaphthalene.

In comparing the action of light on organic compounds we can either estimate the change which takes place in colour, or in the absence of this, by some direct chemical change which is brought about by the action itself. The latter method is of course of a more direct and satisfactory nature than the former, in most cases, although variations in colour are valuable indications that some change is in progress.

As an introduction to the study of this subject the following researches on the general action of light on organic substances are of interest. They indicate the possible nature of these reactions in the case of dyes.

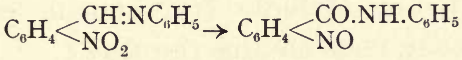
For example, Ciamician and Silber have conclusively shown that this action may give rise to chemical change. Benzophenone dissolved in alcohol is reduced to benzpinacone and aldehyde. Under the same influence the aromatic orthonitrobenzaldehyde is transformed into nitrosobenzoic acid. The action is indicated as follows :



$$C_6H_4{<}\begin{matrix}CHO\\NO_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}COOH\\NO\end{matrix}$$

Here we have an action which leads to the internal re-arrangement of the molecule rather than to decomposition.

Sachs and Kempf (*Ber.* 1902, 2707) have also shown that a similar change takes place with the aniline compound of orthonitrobenzaldehyde. As a result of the action nitrobenzanilide is produced as follows :

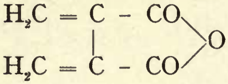


$$C_6H_4{<}\begin{matrix}CH{:}NC_6H_5\\NO_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CO.NH.C_6H_5\\NO\end{matrix}$$

The conclusion arrived at is that all aromatic compounds containing nitro groups in the ortho position are sensitive to light.

From a general point of view this is of interest, the action of the light being sufficient to induce intra-molecular change or migration when the side groups are in close proximity (the ortho position). The mordanting power of ortho-hydroxy compounds probably depends in the same way on the proximity and combined action of the $\left[\begin{matrix}-O\,H\\-O\,H\end{matrix}\right.$ groups, as has been noticed elsewhere.

When the action of light is accompanied by colour change, as it is in many cases, the actions of this class are classified under the term chromotropy. This phenomenon is very clearly shown by the various substitution-products of butadienedicarboxylic acid; for instance of



These compounds are all coloured. They are red, brown, violet, or yellow, as the case may be.

These compounds undergo more or less rapid change under the influence of light. The ultimate effect of this change varies in its nature; it is sometimes permanent and sometimes temporary.

The triphenyl derivative, when exposed to the direct action of sunlight for a few minutes, changes its colour to blood-red. Its original colour is, however, slowly recovered in the dark.

If, however, the first exposure is greatly prolonged, and extends for several days, or even months, the change is of too profound a nature for any subsequent reversal of the action, with regeneration of the original form, to take place.

In this case the final products of the action seem to be two white aldehydes, with different melting-points, but with the same composition, and molecular weight as the original substance.

The yellow diphenyl derivative yields three distinct and colourless aldehydes with different melting-points.

It is not to be supposed, however, that the products of the action of light are always colourless. The dark red piperonyl derivative yields two new aldehydes, which possess great tinctorial properties.

These results indicate that our present view of chromophores must be widened (Stobbe, *Chem. Zeit.* 1904, 919).

The conversion of anthracene into dianthracene under the influence of light is a reversible one. The exact conditions of this change have been examined by Weigert (*Chem. Zeit.* 1904, 923), and Luther and Weigert (*Zeit. Phys. Chem.* 1905, 53, 385), who have found that under definite conditions, and with dilute solutions true equilibria are established. The source of light in the case of these experiments was the electric arc. As a result of this investigation it was found that the amount of dianthracene formed depended on:

(1) The character of the light.

(2) The change is proportional to the light intensity, and the surface exposed, or to the radius of the cylindrical vessels used.

(3) The action is independent of the thickness of the layer through which the light passes.

(4) The action is inversely proportional to the volume of the solution, and independent of the amount of anthracene in solution.

Both the temperature and the nature of the solvent have an influence on the result, and are important factors in determining the equilibrium.

As is well known, the leuco bases of many organic substances are readily oxidisable. Others are relatively stable. The action of light seems to influence these results. If these substances are embedded in collodion their sensitiveness is greatly increased.

This is said to be due to the combined nitric acid affording an additional supply of oxygen under the influence of light. The fact has been noticed also that an addition of quinoline to the collodion greatly increases the sensitiveness to light. We have here, therefore, a second, or foreign, substance influencing the reaction (König. *Chem. Zeit.* 1904, 922).

In these actions it has been noticed that the greatest effect is produced by complementary light. This result seems to be a general one, as noticed later on.

A very decided colour-change which is brought about only in the presence of a third substance, which happens in this case to be a textile fibre, is seen in the following instance. When cotton yarn is padded with a 5 per cent. solution of metatungstate of soda, and exposed to light, a rapid change takes place with the production of a blue colour. This is evidently due to the reduction of the salt. The action is seemingly a reversible one, for if the yarn is subsequently stored in a dark place, the blue shade is discharged.

If the blue fabric, or yarn be immersed in water, the coloured compound is removed from the fibre. In this state, and away from the influence of the fibre substance it gradually resumes its colourless form, even under the influence of strong light. It would seem, therefore, that the presence of the fibre substance is the modifying factor in this reaction.

Turning to the action of dyes themselves under the disturbing action of light, the following facts have been noticed. The constitution of the dye has a great influence on the "fastness" of the dye against light. An elaborate series of direct trials have been made by Brownalie (*J.S.D. and C.* 1902, 296) and as a result the following tabulated conclusions have been arrived at.

(1) The diphenyl base plays little, or no part in the action.

(2) Colours derived from phenol, or its homologues, and their sulphonic, or carboxylic acids are fast to light.

(3) Colours derived from hydroxybenzenes and homologues containing more than one hydroxyl group are fugitive.

(4) Colours derived from the amines of the benzene series, and their sulphonic acids, or carboxylic acids are fugitive.

(5) Colours derived from alpha and beta naphthols, and their sulphonic acids are not fast to light.

(6) Colours from alpha and beta naphthylamines, and their sulphonic acids are fugitive.

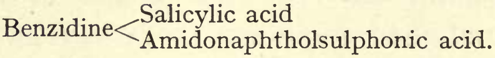
(7) Those from amido naphthols, and their sulphonic acids vary. The 2.6.8 monosulphonic acid, and the 2.3.6.8 disulphonic acids are fast. The 1.8.3.6, and 1.8.2.4 acids are fugitive colours.

(8) The colours from the dihydroxynaphthalenes, and their sulphonic acids agree closely with the corresponding amidonaphthols.

(9) Replacing amido by hydroxyl groups results in increased fastness.

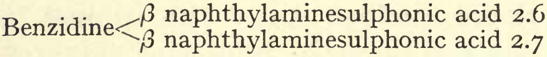
(10) The salt-forming groups SO_3H and $CO.OH$ cause no difference in fastness. The auxochromic NH_2 and OH groups play important parts in the action.

In the case of mixed colours the same rules are followed. If the two separate constituents are fast, so is the dye. This is very well seen in the case of the direct colour Diamine Fast Red F, the composition of which is



$$\text{Benzidine} < \begin{array}{l}\text{Salicylic acid}\\ \text{Amidonaphtholsulphonic acid.}\end{array}$$

If, on the other hand, both are loose, the dye itself will be an unsatisfactory one in this respect. Delta-purpurine 5B is given as an example.



$$\text{Benzidine} < \begin{array}{l}\beta\ \text{naphthylaminesulphonic acid 2.6}\\ \beta\ \text{naphthylaminesulphonic acid 2.7}\end{array}$$

In mixed dyes, that is to say, where one of the constituents is fast and the other loose, the dye generally stands midway between the two in the scale of fastness, but there are many exceptions to this rule.

Three theories have been put forward to explain the cause of this action. They are of an indirect nature, and may be briefly summarised as follows :

(1) *The oxygen theory.*—The dyes under the influence of light interact with oxygen, and form colourless compounds.

Berthollet in 1792 came to the conclusion that oxygen combined with the colours, and made them pale.

The colour at the end of the exposure is, from this point of view, proportional to the resistance to this action.

(2) *The ozone theory.*—The colours are decomposed or altered by the production of ozone (or hydrogen peroxide) in the fibre, chiefly by evaporation of moisture.

(3) *Reduction theory.*—The dye is reduced by cotton fibre, or directly by the action of light.

Experiments conducted in the presence of oxidising agents have given conflicting results. The presence of sodium hydrosulphite solution also gives varying results.

Whatever be the cause of the results obtained in the presence of oxidising, or reducing reagents, it is important to note that dyed fabrics always show an increased fastness against the action of light in vacuo. This effect is very marked.

Similar experiments with sensitive organic compounds are wanting. They should be of equal interest.

A typical example of this action may be seen when cotton dyed with Diamine Sky Blue B is placed in long glass tubes, which are subsequently exhausted by water suction to a pressure of 10 mm. (9 mm. of which are due to water vapour), and exposed for fourteen days to bright light. The shade remained absolutely unchanged. A comparison trial, which was exposed to the light side by side with the other one, but under ordinary conditions, had entirely lost its colour. The cotton was quite white.

The same blue cotton sealed in a tube in an atmosphere of oxygen gas lost its colour even more rapidly than the above comparison sample. On the other hand, the colour remained unaltered in an atmosphere of either hydrogen, carbon dioxide, sulphur dioxide, or coal gas. When exposed in nitrous oxide gas the effect produced was very similar to that noticed in the case of oxygen.

It is evident, therefore, that dyed samples in the absence of oxygen will not fade.

Berthollet in 1792 noticed that the fading action of colours seemed to be intensified in the presence of an alkali. In the same way an acid condition seems to retard the fading action.

The fact that the fading is intimately connected with the presence of oxygen may, therefore, be taken as established. It remains to trace the actual action which takes place. It has been noticed that the evaporation of water at ordinary temperatures leads to the formation of ozone in very small quantities.

The fading of the colours may, therefore, be due to the direct interaction between the ozone, or hydrogen peroxide so formed, from the oxygen in the air; colourless compounds of unknown composition being produced. The action seems also to be proportional to the moisture present at the time of the experiment.

Under the influence of the light vibrations the oxygen molecule may be more readily split up, and an action of the following order induced :

$$O_2 \rightleftarrows O + O$$

and this may take place more readily when the oxygen is associated with water molecules.

Whatever the action, the result is clearly seen in the alteration in colour.

The most favourable atmosphere for this fading action is a hot, moist, and alkaline one.

It has also been noticed that the presence of such seemingly inert substances as alcohol and pyridine vapour will greatly influence the rate of fading. It is greatly accelerated in their presence.

Although our knowledge is incomplete, we may at least assume that the action is a very complicated one, and beyond recording certain facts, we are confined to most indefinite speculations.

The influence of the fibre is also a factor to be considered. All fibres do not act in the same way. The fastness of the same dye varies on different fibres. Methylene blue on cotton is faster than on wool. Indigo on the other hand gives more fugitive shades on wool than on cotton.

Colours dyed on cotton, oxycellulose, trinitrocellulose and jute are said to be all equally fast. This might be put forward as an argument that there is no chemical action in dyeing these fibres, the dye being present in all cases in the same state. On silk eighty-four per cent. of the colours experimented with showed no difference ; sixteen per cent. were said to be slightly faster.

There are therefore three factors, at least, which may, under these same conditions, influence the rate of fading, viz., the physical condition of the dye in the fibre, that is to say, its state of division; the possibility of some chemical action between the fibre and dye, and the transparency of the fibre substance in its relation to the passage of the light rays.

The statement that cotton colours are fast in solution, but not on the fibre, is not correct.

The general conclusion arrived at, therefore, in the present state of our knowledge, is that the action is an oxidising, and not a reducing one. In the absence of oxygen there is no change in colour, due to the *direct* action of light. The action is also proportional to the moisture present on the fibre. It is clear also that the constitution of a colour determines its stability.

An advance in our knowledge of this subject was made by Dépierre and Clouet (*J.S.D. and C.* 1885, 245), when these authors discovered that the action of light depended upon its nature. It might be expected that the so-called chemical rays would have a greater efficiency in this action in the same way that they have a greater influence in the decomposition of photochemical salts. As a matter of fact, this is not the case. It must, however, be remembered that we have here a disturbing action in the case of dyes, due to colour-filtering effect. This natural screen may therefore in its action veil, or modify, the original effects of the light. The most active rays may only have a chance of acting superficially in some cases, at any rate, and, therefore, have their normal action incidentally modified. Less active rays which are passed on through the superficial screen may actually have a greater cumulative effect.

Dufton (*J.S.D. and C.* 1894, p. 92) has shown that in any case the waves which are most readily absorbed are the most active ones. That is to say, the colours complementary to those reflected produce the greatest effect. This seems to be a general law. The absorption of rays may, as in the cases given at the beginning of this chapter, produce a state of strain in the dye molecule leading to a different state of equilibrium, or formation of fresh compounds, and apart from this the formation of active "oxygen" compounds would seem to bring about the change in the dye which leads to the change in colour. Assuming the quinonoid theory of colour, it would be necessary to allow that the structure of the dye molecule is profoundly modified.

The whole subject is of extreme importance to the dyer, and should receive more attention.

For instance, it has been generally allowed that the basic colours produced on an antimony tannin lake are fast as compared with those on tannic acid itself. This action is an obscure one, and hardly agrees with the contention that dyes in the presence of acids are faster against light.

It has been stated elsewhere that the action of light is an important factor in the dyeing of Turkey Red on cotton.

Another case of the influence of light in the process of dyeing is that noticed by Pokorng (*Bull. Soc. Ind. Mulh.* 1893, 282). Wool and silk "dyed" with naphthylamine become darker in shade on exposure to light. The shades produced by subsequent treatment with nitrous acid are also much darker than those from the original skein. The action of light on diazotised primuline or silk has even been made the basis of a photographic process by Messrs. Green, Cross and Bevan and Farrell respectively.

There is clearly plenty of scope for further research on this interesting and almost untouched branch of the subject.

The action of light on the natural colouring-matters present in the vegetable fibres is well known. It is taken advantage of in the bleaching of linen, and was at one time universally used for this purpose.

In the case of cotton the action is greatly increased if the fibre is previously treated with a soda dye-bath. Such a sample will be well bleached before the other one is appreciably lightened in colour, under the same conditions.

The fact has been recorded that some dyes in solution will dye the glass containing vessel to a far greater extent on the side which faces the light. This is possibly due to the more solvent action of the water on the glass in the presence of light, or even to its decomposition, rather than any action in the dye itself. The action seems to be a very slow one.

To the student this subject is an absorbing one. It may be attacked either from the point of view of the fibres, or from that of the reactions which take place when light acts on organic compounds. In either case important results must follow a careful study of the subject.

Two changes which take place under the influence of light rays, and which are both connected with indigo, are of interest.

The first is that noticed by Kopp (*Bull. Soc. Ind. de Mulh*). Kalle's indigo salt is very sensitive to light when present as the bisulphate compound. A dyeing process has even been founded on this fact. The nature of the reaction is unknown.

The second is that benzylidineorthonitroacetophenone is converted into indigo by the action of light by intermolecular oxidation. No action takes place in the dark, very little in the red rays, more in the green, and the influence reaches a maximum in the violet (Engler and Dorant, *Ber.* 28, 2497). The inference is that the action is closely connected with the presence of the chemical rays.

The student might also refer to some work done by W. Straub (*Archiv für Exp. Path. und Pharm.* 51, 383), on the action of light on eosin under special circumstances.

The complete decolorisation of this dye required

65 molecules of oxygen. The action is ascribed to the production of eosin peroxide in the case in question.

It will be remembered that the fastness of lakes depends on the nature of the "absorbing" material. Quite recently W. E. Evans (*Eng. Pat.* 19795, 1905) has shown that light influences the drying of materials. It is said that the action may either hasten, or retard this operation according to its nature.

CHAPTER XII

METHODS OF RESEARCH

It is considered advisable for the benefit of students and others, who contemplate starting original work on this subject to outline briefly the methods used by previous workers, so far as they have been published.

The methods used are simple in their nature, and in many cases are similar to those used in the practice of dyeing.

Direct weighing method.—The fibre is carefully weighed on a chemical balance, before and after, the experiment.

The process is not, as a rule, a satisfactory one. For instance, it has been used to record the actual gain in weight of fibres which have been mordanted under different conditions. The net gain in weight is registered, and this, perhaps, in ordinary dyeing, mordanting, or weighting, experiments may be satisfactory, yet the *actual nature* of the addition in many cases, can be only guessed at, or is even unknown.

This must be determined by actual chemical analysis. This, in many cases, is a very difficult operation, and entails the elaboration of special methods.

It is probable that in the future such a rough and ready method of estimation will receive little support except, of course, in cases where the reaction between fibre and substance absorbed can be readily ascertained, and is beyond question. For instance, it might be a satisfactory method of showing the different results obtained by the treatment of silk with pure tannic acid. On the other hand, it would be a very unsatisfactory way of indicating the action of silk on stannic chloride solution, or wool on bichromate solution. Any further experiments on the action of mordants, can have very little value, if they are simply of this nature. The composition of the salt fixed must be clearly determined, and any alteration in the composition of the mordant solution itself, noted.

The condition of the fibre, in these experiments may have a disturbing effect on direct weighing. The percentage of moisture must be estimated, and allowed for.

This method is not satisfactory in the case of dyeing with aniline colours, unless they are present in large quantities. Even here, it is advisable to check the amount of dye left in the solution, by processes mentioned further on in this chapter.

Much of the present uncertainty of the reactions in dyeing, is clearly due to the primitive nature of many of the recorded experiments. Such a state of affairs would not be tolerated in any other branch of chemical or physical work.

The conditions of the fibre state must not be allowed to vary without record. Perhaps the most difficult problem in connection with such work is the standardising of a fibre state, which shall be constant and easily reproduced at will. Such treatment as is generally adopted in practice, which may entail the use of solutions of acid or alkaline reaction, is of a doubtful nature.

The action of such reagents is disturbing and specific and, with our present knowledge, it is impossible to estimate their influence on the fibres, with any certainty, or indicate their effect on the absorption values.

Ultimate analysis.—This is only satisfactory in rare instances, for the reasons which hold in the above case.

It may be used to estimate the percentage of nitrogen in silk. The percentage present in the fibre is 17.6. The greatest care must, however, be taken to exclude the possibility of any other nitrogenous substances being present, and so interfering with the result.

Persoz (*Monit. Scient.* 1887, 597) suggests that silk be reduced to a powder after treatment with 30 per cent. hydrochloric acid. The nitrogen factor is then increased to 18 per cent. The advantage of this procedure is doubtful.

Estimation of ash.—This may be useful to indicate the presence of mineral matter in the case of the absorption of inorganic mordants. The composition of the ash should, however, be determined and the possible action of incineration on its composition allowed for.

Direct analysis.—Wherever possible this method should be adopted. For instance, if this method had been used throughout in Heermann's experimental work on the action of mordants the results obtained would have been of greater value.

The work necessary to devise special methods of analysis to meet the requirements of the work is often of a tedious nature. It may even be impossible to devise such direct methods of determining the actions involved, but whenever possible they should be used. The methods in use for ordinary analysis are, of course, available.

Acidimetric methods are useful to estimate acids, alkalies, and the absorption of these substances by fibres, if special precautions are taken.

In some cases acid colours may be directly estimated by a standard solution of Night Blue.

In the same way tannic acid is said to give good results when used to estimate basic colours.

Knecht has recently recommended the use of titanium salts for the volumetric method of estimating dye-stuffs in solution (*J.S.C. and D.* 24. 154). This should be useful in many cases.

The estimation of alizarine and mordant colours is a difficult operation. Their "mordant value" may be obtained by the method suggested by the writer (*J.S.C.I.*, 12, 997).

Solvent action of reagents.—This has been used to indicate the way in which colours are held by fibres.

This method was adopted by the writer to determine the relative "fastness" of ingrain and direct dyed colours. Other cases will also have been noticed where this method is made use of, particularly where alcohol has been used to extract dye from the fibre. Benzene, and amyl alcohol, have also been used for this purpose with success.

Direct colour estimation.—The numerous tinctometers in vogue may be used for this purpose. With the Lovibond instrument a direct colour-record may be kept of any dye solution. It may even be used for the estimation of dyes on fabrics.

Mills and Hamilton used the tinctometer to estimate the relative absorption of dyes by fibres.

This method is a very accurate one when the amount of colour present in a solution is small.

Estimation by dyed sample.—A shade is matched by direct dyeing on the same fibre under standard conditions. This method is useful in cases where the dye-bath is exhausted.

Relative dyeing properties of fibres.—This may sometimes indicate changes like those which take place during the mercerising action, or in the nitration of cotton fibre.

Thermochemical reactions are recorded by special means, and involve the use of a calorimeter.

Dissociation and association effects in solution.—The student is referred to the standard books on physical chemistry for information on this subject.

Temperature.—The control of the temperature during experiments in dyeing is often of great importance. This may be effected by the use of a thermostat.

Spectroscopic examination.—Formánek recommends this process of analysis for the detection of colouring-matters, particularly of the variations in colour noticed after treatment with certain reagents, such as ammonia, nitric acid, &c.

Polarised light.—Chardonnet has used this method to distinguish the different states of nitration in nitrocellulose.

Hübner and Pope indicate that they are using this to indicate change in the fibre state during the process of mercerising.

To a great extent the investigator must be guided by the problems before him, and the general and recognised methods of analysis should be utilised wherever possible to the exclusion of such tests as the mere weighing of the fibres before and after treatment, or comparative dye trials.

The student should make certain that whenever possible his work shall be of a quantitative nature, and that the conditions of the experiments are accurately recorded.

Special attention should be given to reactions which take new directions or are modified in the presence of fibres.

Such particulars as deal with the physical constants of solutions must be sought for in the recognised text-books on the subject.

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