Colours, Stains, and Dyes.¹

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THE great majority of chemical substances occurring either as natural products or as the outcome of synthetic preparations in the laboratory are colourless. In other words, white light reflected from their surfaces or transmitted through these solutions is unaffected so far as its balanced colours are concerned and emerges unaltered. The absorption of light in these cases is general; that is, it takes place equally throughout the visible range of the spectrum and the object, therefore appears colourless.

On the other hand, there are a number of substances which possess the property of absorbing certain portions of the visible spectrum while reflecting or transmitting the remainder. These substances, therefore, appear to the eye to be coloured in accordance with the portion of the spectrum transmitted or reflected. A red substance is one which absorbs the blue region of the spectrum; a blue substance one which absorbs the red region, and so forth. This is known as selective absorption. Again, there are a number of substances, chiefly members of the carbon family, which have the power of absorbing rays outside the visible region of the spectrum—for example, in the infra-red or the ultra-violet—and these substances, since they possess selective absorption, must be regarded as coloured in a chemical sense, although the "colour" they transmit or absorb is not visible to the eye.

The hydrocarbon benzene is an example of the type of chemically coloured substance, and, as we shall find later, this property possessed by benzene causes it to be the parent substance of those very numerous and industrially important materials—the coal-tar dyes.

It is not in its lack of power to detect the ultra-violet range alone that the eye fails as an organ of vision, because even in the visible region its power to detect the end colours is seriously restricted. It is most sensitive towards green and red.

The power of a chemical substance to produce selective absorption is without doubt due to its chemical structure; that is to say, white light is "filtered" through the molecular structure of the substance, leaving a "portion" behind in its passage. The colour is therefore dependent on the chemical composition of the particular compound. On the other hand, it is possible to produce visible colour by entirely physical or mechanical means, as, for example, by ruling a number of fine lines on glass, and in these cases colour is independent of chemical structure, being entirely physical in character.

Nature, in producing the variety of coloured substances around us, has adopted both the physical and chemical methods to achieve her ends. The colour of flowers and leaves has been brought about by the use of coloured chemical substances, and these I shall deal with later. But many of the colour effects produced in the wings and feathers of birds and in butterflies are not due to the presence of any coloured substance in them, but to the arrangement of fine filaments or hairs, which serve the purpose of disintegrating white light and reflecting the desired shade of colour. The best

test for this kind of colour effect is to examine the coloured object by transmitted light. If no colour is transmitted the reflected colour is probably due to physical causes.

A considerable number of the chemical substances which owe their colour to structure are inorganic in origin, and the colours depend mainly on the presence of some colour-producing metal; for example, chromium, cobalt, copper, and so forth. They are mostly used as pigments for the production of coloured surfaces by painting, or for the production of coloured decorations on china. Of these I do not propose to make any mention, not because they are unimportant as coloured substances, but because they do not trace any relationship to the stains and dyes which belong to organic chemistry, and are bound up with the recurrence of one particular element, namely, carbon.

There are some 300,000 definite compounds of carbon known, and the activities of research chemists add, perhaps, 4000 to these yearly. The majority of these compounds are colourless in the sense that they give only general absorption throughout the visible region of the spectrum. Some are, however, coloured—that is, they give selective absorption within the visible region—and it is evident that in these cases the colour cannot be ascribed to the presence of some particular metal, as with the metallic pigments, but must be due to some special condition of the element carbon. As a matter of fact, it is due to what is known as the "unsaturated state." The greater number of known compounds of carbon are "saturated" in the sense that all affinity which the carbon atom possesses for the atoms of other elements is fully satisfied. This is the case when carbon combines with hydrogen to form methane CH_4 , or when it combines with oxygen to form carbon dioxide CO_2 . No carbon compound of this type possesses colour, and every "saturated" compound shows general absorption of light. It is possible, however, to cause carbon to combine with carbon by more than one valency, and in such a case a condition of "unsaturation" arises:

Ethane (saturated). Ethylene (unsaturated).

The affinity of each carbon atom is no longer satisfied by its proper quantity of hydrogen (or oxygen), and since there is naturally always a tendency for the substance to acquire the hydrogen atoms necessary for saturation, the "unsaturated" condition is definitely less stable than the saturated state.

The presence of one unsaturated linkage does not, however, confer colour on an organic compound—at least two being necessary for the purpose. It is also necessary that the two double linkages should be separated by one single linkage. This is known as the conjugated system of double linkages, and its presence in an organic compound apparently confers on it the property of producing selected absorption in the visible

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region of the spectrum. The simplest possible coloured organic substances are therefore glyoxal and diacetyl:

These substances, however, although they are of great interest as showing the origin of colour in organic substances, are relatively unimportant owing to their slight colour and their rarity. It is to the derivatives of the hydrocarbon benzene, upon which is based the chemistry of the coal-tar colour, that special interest attaches.

As already mentioned, benzene shows selective absorption in the ultra-violet region of the spectrum, and is therefore visibly colourless, although, chemically speaking, it possesses marked colour. The great number of the derivatives of benzene are, therefore, visibly colourless, but the chief point which has to be remembered is that, although visibly without colour, these derivatives possess potentially visible colour, and it is always possible to produce visibly coloured substances from them by modifying the molecular conditions which lead to the selective absorption causing visible colour.

The organic chemist's conception of the structure of benzene is still that which was propounded by Kekulé some seventy years ago, and it is fair to say that no theory, either physical or chemical, has been brought forward since then which can be regarded as quite adequate. Kekulé regarded benzene as a substance containing a conjugated system of double linkages, upon which the colour of organic substances depends; but in order to account for the peculiar properties of benzene, its remarkable stability, and the formation of its derivatives, it is necessary to postulate a symmetrical formula which is expressed either by the Armstrong formula or by the simple hexagon—a necessity, which was met by Kekulé by the supposition that there was rapid dynamic interchange between the two unsaturated individuals of his formula. Below are given the forms of linkages which have been given to the benzene molecule, the carbon atoms, assumed to occur at the points of the hexagon, being omitted:

This dynamic interchange, leading to symmetry, is expressed both by the Armstrong formula and by the conventional formula, but it is evident that each of them is merely a compromise, and represents an intermediate condition between two rapidly interchanging forms. They do not mean more than this, because any condition which postulates the existence of trivalent carbon has to contend with a number of cases in which the occurrence of this condition leads to

instability quite out of keeping with the remarkable stability of benzene and its analogues and derivatives. This is the case with triphenylmethyl and similar compounds.

The dynamic conception of the structure of benzene supplies a reason for the recurrence of the strong ultra-violet absorption which is characteristic of this substance. Moreover, it suggests that if it were possible to modify the conditions leading to this absorption, it might be possible to throw the absorption within the visible range of the spectrum, and thus produce visible colour.

The simplest visibly coloured member of the series is quinone, which is produced easily from hydroquinone by oxidation and is reconverted into hydroquinone on reduction:

Here, then, at any rate, we have one means by which we can produce visible colour from a benzene derivative. There are certainly other means, but these are not as yet so clearly defined, and there is no question that when H. E. Armstrong propounded his quinone theory of colour he enunciated the fundamental principle on which the chemistry of the coal-tar colours is based. For there can be no doubt that the colours of these compounds are due to the presence in them of a quinone residue, which, acting like the simplest quinone ring shown above, throws the ultra-violet absorption of the visibly colourless benzene derivative into the visible region of the spectrum.

This is easily shown by the conversion of the visibly colourless phenolphthalein into its coloured alkali salt. However, it is a simple matter by altering the groups present to throw the absorption into any portion of the visible spectrum required, and thus to obtain any desired colour. The chemist is able, therefore, while retaining the same skeleton, to produce any colour at will by merely altering the nature of attached groups.

The name coal-tar colour is derived, of course, from the fact that the parent hydrocarbons from which the colours are derived—the benzene hydrocarbons and their analogues—are obtained by the distillation of coal-tar. The first of the series, mauveine, was discovered by the late Sir William Perkin in 1856, in an attempt to prepare the alkaloid quinine synthetically. But Perkin did more than discover a new series of colouring matters. He also introduced a new method of dyeing. Up to that time, dyeing had been a composite process involving the actual formation of the coloured substance on the fibre itself. The two chief processes in use were (a) that of vat-dyeing and (b) that of mordant dyeing. The first, represented by indigo dyeing, involved the reduction of the coloured substance (indigo) to indigo-white, a material soluble in alkali; the steeping of the fibre in the solution and the reproduction of the insoluble dye by means of the

oxygen of the air. The second required the previous impregnation of the fibre with a metallic hydroxide and the subsequent formation of a coloured lake on the fibre by steeping the prepared material in a dyestuff (alizarine) capable of yielding such a lake.

In each case, therefore, two distinct processes were involved. In the process introduced by Perkin only one operation was necessary. The dye contains, as already mentioned, a quinone or quinonimine residue, which causes the dyestuff in the form of its salt to be soluble in water:

It happens that the coloured base is soluble in the wool fibre, and when the fibre is added to the dye-bath the coloured base is extracted, leaving the mineral acid free in solution. The operation is of the same order as that which determines the extraction by, say, ether of an organic substance soluble in water. The coloured base is not, however, soluble in cotton, and hence this material is not coloured in the dye-bath.

These are known as the basic dyes; and a similar effect is produced by the acid dyes, although, since these are the sodium salts of sulphonic acids, the dye-bath has to be rendered acid previously in order to liberate the free sulphonic acids, which then dissolve in the substance of the wool. Cotton would not, of course, be coloured by this process, although, as it was found that the new basic colours possessed the power of giving an insoluble coloured compound with tannic acid and an antimony salt, it was possible to affix them to the cotton fibre by a two-process method, involving the previous treatment of the material with tannic acid and tartar emetic.

It was not until twenty years later that it was found (Böttiger, 1886) that a certain type of azo-dye derived from benzene possessed the property of being soluble in the cotton fibre, a discovery which led to the preparation of the large number of substantive cotton dyes known at the present day. In this case it is the sodium salt of the sulphonic acid which is extracted. This discovery was entirely accidental, but, as so often happens in organic chemistry, it was found that the property was possessed by a large number of substances of the same type, or having the same skeleton formation, and, since it is possible readily to alter the shade by varying the nature of attached groups, the series contains representatives of all shades of colour.

It must be remembered, however, that there is a marked difference between the two methods of dyeing—one, the older method, in which the dye is formed in the fibre, and the other, the newer method, in which the fibre acts merely as an extractor for the coloured base, acid, or salt. It is evident that, other things being equal, the older processes should give the faster dyeings; that is, the colour would be more firmly fixed in the fibre and less likely to be affected by the various conditions, such as exposure to light, washing, etc., to which a dyed fabric has usually to be subjected. This is, as a matter of fact, the case, and numerous processes have been devised by which the stained fabric (as I prefer to call it) can be rendered more fast by after-treatment; that is to say, by causing another colour to

be produced in the fibre from the colouring matter already there. One of the best illustrations of this is the method by which an azo dye can be produced on the fibre from a stained fabric which has been stained by a substance having an NH_2 group:

There are many other methods, such as after-treatment with metallic salts, or with formaldehyde, which can be employed. Indeed, such processes would be still more necessary were it not for the remarkable tenacity with which the stained fabric, in many cases, retains its stain. The affinity varies in different cases, both as regards the power and speed of absorption, and is probably connected with the size of the molecular (colloidal) aggregates which are present in the dye-solutions. It is not connected with the actual molecular weights.

Nevertheless, although there are some stains which possess so marked an affinity for the fibre as to render them comparable with true dyestuffs (those produced on the fibre) in fastness, and some which lend themselves to after-treatment, and fall therefore within the category of true dyestuffs, there are a large number which possess all the inherent disabilities of the class; that is, they are unsaturated organic compounds tending to pass into the saturated (colourless) state under favourable conditions. Such conditions are always present in the oxygen of the air, which in the presence of light constitutes a formidable opponent to all coloured organic compounds. As already mentioned, Nature got over this difficulty in the case of bird's feathers and butterfly's wings and also in the wing cases of coloured beetles by ignoring the organic colour altogether. She utilised them, however, in the case of the flowers, but chose substances highly oxygenated in structure, which would be least likely to be affected by air and light. For example, the colour of the red rose is delphinidine,

and this is also the basis of the colour of the blue cornflower, the only difference being in the character of the group attached to the oxonium oxygen.

However, as the science of organic chemistry advanced, it became possible to contemplate the synthetic preparation of some of the natural colouring matters, of which indigo, alizarine, and logwood were types. These are not natural colouring matters in the sense that they are used by Nature as such, but have been evolved by man for his own purpose by a process of trial and error. They represent the survivors of a vast number of natural substances with which man must have experimented throughout the ages in order to produce colour for his own purposes. Together with certain mordant colours derived from lichens, which are still used for dyeing in certain parts of the country, they constituted the sole means of producing

dyed fabrics at the time when the coal-tar colours were discovered. Their value as dyestuffs was without question, the world's yearly consumption of indigo alone, at that time, representing some 4,000,000*l*.

It must also be remembered that it was not the question alone of the commercial production of the dye in competition with the natural product which was sought, because this must have appeared a totally impracticable problem in those early days. It was rather the search for the reason why alizarine was a mordant dye and why indigo was a vat-dye which was the incentive to research, because when these facts were discovered other substances having similar properties could be prepared. The attack in every case followed the usual lines. In the first instance, the structure of alizarine (the mordant dyestuff of the madder root) was revealed by analysis, when Baeyer found that it gave anthracene on distillation with zinc. Its synthesis from the anthracene of coal-tar followed in the next year, being effected almost simultaneously by Graebe and Liebmann in Germany and by Perkin in England. In this case the preparation was so simple and the raw material so easily obtained that the natural madder industry was rapidly killed. The determination of the formula and synthesis of alizarine showed the

particular grouping, namely, $\begin{array}{c} \text{CO OH} \\ \diagdown \quad \diagup \\ \text{OH} \end{array}$ on which

mordant dyeing depended. Hence the preparation of a large number of analogues of varying shades of colour followed.

The determination of the structure of indigo took longer, and occupied Baeyer at Munich some eighteen years. In this case the colour was synthesised and manufactured on a commercial scale three years before its structure was determined, because, as sometimes happens, a reaction, the course of which was then unknown, led to the formation of the dye. Here, again, the determination of structure showed that the

property of vat-dyeing depended on the presence of

the grouping $-\text{C}=\text{C}-$, and in consequence, whereas blue indigo was the only known member of its class in 1890, at the present day every shade of colour is represented in this particularly fast series.

Finally, at the beginning of the present century, the accidental discovery of indanthrene by Bohr placed on the market the first member of a series of vat-dyes, which constitutes without question the fastest series of colouring matters hitherto prepared. Practically all shades of colours are represented, the principle of dyeing being essentially the same as that of indigo.

Before the War we relied mainly on Germany for the production of our dyestuffs, and, what was still more serious, we left to them the research work on which the production of new dyestuffs depended. Dyestuff chemistry is merely a branch of organic chemistry, which includes also the preparation of organic chemical substances used in a variety of industries essential in peace and war. The possession of a dyestuff industry implies, therefore, the possession of a band of trained organic chemists and, what is more important, the possession of university and university college laboratories, where organic chemists can be adequately trained in methods of research. As a member of the Dyestuffs Development Committee, it has been my good fortune within the past six months to visit all the dye-producing factories operating in Great Britain, and I have been struck with the very real success which has attended the efforts of the past five years to establish the industry. If we had merely reached the level of excellence attained in Germany before the War, the fact would have been very creditable, but we have done more than this, and in several cases, notably in the production of a new indanthrene green, we have already drawn ahead; a position, it is to be hoped, we shall not again lose.

Some Geographical Aspects of the British Empire Exhibition.

THE British Empire Exhibition at Wembley, in the north-west outskirts of London, strikes at once a note on the Empire as a unit. From the Palace of Engineering, with its sense of the fullness of the metallurgical industries of Britain, across the way to the Palace of Industry, almost crowded out with the multifarious products of Britain's factories, one gathers an impression of diversity as shown by fountain-pens and gramophones in contrast with big guns and giant railway engines, of high quality from the silks and laces to the coach-work on the motor cars, of stability from the various types of safe and strong room to the giant turbines; and, withal, there is a feeling of much energy crowded into a tiny space. Visit may succeed visit to these two great palaces, the main monument to the occupations of Britons at home, and yet their innermost recesses, their by-ways, and their out-of-the-way corners would not all be explored; it would appear that the visitor is left deliberately with few indications of the wealth of British products here housed, for each visit brings to light something previously missed and leaves the thought that there is yet something more to find.

The British Isles are thus presented as a crowded hive of industry, and this impression is intensified when one penetrates below the surface. Mannequin parades, exhibits of machine processes in cotton, paper, and so forth, are co-operative efforts; they are not labelled as the work of one firm or as, necessarily, the product of one district; they are specimens of Britons' work. The student of geography who wishes to emphasise or correct his book-lore is driven to much mental effort to analyse the contents of these great buildings, to sort out the products, say, of the Black Country and to localise the various elements of industrial Britain. Except in a few instances, mainly in the food section, the visitor is not asked to buy, and the exhibit is not primarily designed as an advertisement; in this respect the student would penetrate deeper and more easily into the mysteries of British manufactures at one of the annual trade shows, such as the British Industries Fair or the Motor Show. Of course, customers from overseas can get into touch with manufacturers, but the trading element, the business of selling the goods, is kept in the background; here is primarily an exhibit of what