

Old Dyestuffs and New Textiles and New Dyestuffs and Old Textiles

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Vortrag, gehalten am XI. Internationalen Kongreß für reine und technische Chemie
in London, am 22. Juli 1947*

When I was asked to speak on old Dyestuffs and New Textiles by Mr. Dickie, I was rather hesitant because the scope of such an undertaking is so wide that it seems almost impossible to deal with it in a short lecture. Moreover there are so many topics in the field of textile chemistry that I think that a survey must necessarily be a sketch which omits many important points. I shall therefore try to show how textile chemistry has changed during the last 50 years, and in what direction the development goes.

My task is also difficult because in England there has been so much excellent research going on during the last 20 years that it seems strange that a foreigner should be asked to tell English chemists what they have done on the field of textiles and dyestuffs. Moreover the "Journal of the Society of Dyers and Colourists" has no equal, and F. M. ROWE'S achievement as an editor is so outstanding that we can only wonder how it was possible that he could manage to go through the war without diminishing the standard of his journal.

It is therefore impossible to deal with the matter without constantly pointing to the papers which have appeared in England on the subject. I shall consequently refer many times to these articles, and it would be impossible to do without them. As everything that I have to tell is well known to you I shall try to find out what are the consequences of the new standpoints which have been developed during the last 50 years, and I shall try to show what can be done in the future. I shall not give many references and details because this would lead much too far and, moreover, the references would only give you facts which are already known to you.

The great many inventions which are known to every student of textile chemistry, are so numerous that it is impossible to mention even the more important ones. Many of them have no practical value and are soon forgotten.

Since the discovery of Mauve by W. H. PERKIN in 1856 the change in dyestuff chemistry has been continuous. Dyestuffs come and go as if they were living beings. GEORG KRAENZLEIN the excellent chemist at Hoechst has described this "Coming, Being and Dying of Dyestuffs" in his well known lecture in the year 1935, and later the regretted F. M. ROWE has given a survey of the dyestuffs during the last 50 years (London 1938). I do not need therefore to dwell on matters which have already been described in a masterly form.—One of the first lectures on the history of dyestuffs was given in 1879 by W. H. PERKIN.

It was entitled "The History of Alizarin" and is an excellent example of how matters should be represented.

On the other hand it may be interesting to consider dyestuffs together with their application because here there are problems which still wait for solution.

Amongst the old dyestuffs which are still used, Indigo made artificially plays an important role. In fact it has still no real rival. Its use has been improved by the new dyeing methods, and with the introduction of hydrosulfite and the Indigosols Indigo seems to hold its place for a long time.

The other natural dyestuffs lost their former importance. Alizarin, once one of the most important dyestuffs, has practically disappeared in spite of the fact that we have so far no real substitute. Alizarin has gone because of its troublesome application, and also because it cannot be easily combined with the modern dyes which want different dyeing methods. Moreover, Alizarin cannot be easily discharged, and the *white* obtained by discharging with the modern chemicals is yellowish on account of the oil used in this process. Even if it would be possible to produce Alizarin Red in one hour this beautiful dye would not meet the demand of the modern dyer. The combinations made with the well known Naphthol AS brands have replaced Alizarin which for many hundred years was the best and is still the best red dye we have at our disposal. Even in Switzerland where there were about 40 Alizarin plants there exists only one firm which makes Alizarin Red, and only one which prints this dye.

The other natural dyes are disappearing. Cochineal is no longer used in the textile trade. It is used for lipsticks and also for dyeing tomato preserves. I have visited in Los Angeles U.S.A. a factory which used 500 pounds of cocheneal carmine a day. Times have passed when the elegant ladies wrote their letters with carmine ink.

Natural dyes are going and even the most beautiful of them, the Tyrian Purple, the most brilliant violet vat dye is scarcely known to the textile chemist. Could it be made cheap enough it would hold its place amongst the best modern dyes we know. I may perhaps recall the fact that Alizarin and the important Azo dyes have been discovered in England. PETER GRIESS, a brewing chemist, was the

* Der Vortrag, der sich ausgesprochen an ein englisches Publikum richtet, wird im Originaltext wiedergegeben. Der Autor ist sich dabei bewußt, daß sein Englisch stark schweizerisch gefärbt ist, und bittet den Leser deshalb um Nachsicht.

first to make and to describe the Azo dyes in Burton-on-Trent.

The science of dyestuffs is closely related with KEKULE'S theory of the quadrivalency of carbon and the theory that benzene is a ring compound. It is remarkable that the first of these fundamental discoveries has also been made in England on the top of a Bus between Clapham Common and London!

I have said already that the development of the artificial dyes has been discussed recently, and I shall therefore refrain from going into details. The facts are known to every student of the field.

Before discussing the new developments in detail we must consider how dyestuffs and textiles are interrelated. During the last 60 years new textiles have been invented which have very different qualities as compared with the old natural ones. It is therefore necessary to discuss these differences because they give a hint what has to be done in order to improve the methods used in dyeing and finishing.

As long as cellulose was simply considered a so-called *colloidal matter* not much could be done with this substance from a scientific point of view. Only when it was found that cellulose is a large molecule and not a particular substance¹ chemists could deal with this highly interesting compound.

Now natural fibres such as cotton, linen, ramie, hemp, wood cellulose, etc. are distinguished from the new textiles by their great *molecular weight*.

The highest molecular weight is found in Ramie which has the empirical formula $(C_6H_{10}O_5)_{2600}$, and this large molecule has very different qualities compared with rayon whose molecular weight is about 7 times smaller. But cotton also is very superior with regards to its molecular weight as compared to the artificial fibres. Cotton has a degree of polymerisation of about 2400, whilst wood cellulose reaches only about 800.

There are still further differences between the natural fibres and the artificial ones. The natural ones have a peculiar submicroscopic structure of their own. The small units are not only orientated parallel to the fibre but they have at the same time a *twist* which accounts for their elasticity and textile strength. This peculiar twist of cotton makes that the submicroscopic elements are turned in such a way that per inch there are about 1000 turns, or per yard between 10 000 to 40 000². No artificial fibre has this characteristic. On account of the great molecular weight and also on account of this curious twist the colloidal properties of natural fibres differ fundamentally from any artificial fibre, the orientated artificial fibres not excluded. These are orient-

ated parallel to the axis but they have no twist and lack therefore the necessary elasticity.

The men engaged in the production of artificial fibres are of course very well aware of the facts underlying the physics and chemistry of cellulose, but so far no possibility presents itself as to how the internal structure of artificial fibres made from cellulose can be made identical with native cellulose. In fact all we can do is to desintegrate the cellulose molecule still more because it is not possible to produce cellulose fibres even from wood cellulose which has a too large molecular weight.

The methods of producing fibres which have a certain orientation date back as far as 1901³ when cuprate fibres were made. In this case it was comparatively easy to stretch the fibre during its production, and Bemberg Silk or Glanzstoff was for some time the best material on the market. When it was found that it was also possible to orientate viscose silk (rayon) Bemberg silk practically disappeared from the market. You know that in recent times new methods were invented which allowed to stretch the fibre very much. Lilienfeld Silk and Fortisan made their appearance and these fibres show great advantages as compared with the old types of Rayon⁴, Durafil, Fortisan, Tenasco, etc. These highly orientated textiles have a strength approaching even linen and ramie, but in account of the absence of any turn or twist these interesting fibres have practically no elasticity. The great problem which arises is: Will it be possible to invent a process which produces the turn as observed in natural fibres? As far as I can see there is no hint to the solution of this allimportant problem. The idea to rotate the orifices which produce twisted fibres at a speed of say 1000 turns a second seems absurd. But we have seen so many astonishing achievements on the field of textile spinning that I should not be astonished if some clever engineer should solve the problem by using a *high frequency* field to produce some effect similar to the natural textiles. This seems rather utopic, but I may say that I am quite optimistic with regards to technology.

As long as, however, the inner structure of our new textiles are not in principle very similar to their natural competitors things remain unsatisfactory in spite of the new inventions which very often prove to be not as good as we read in the textile journals.

It will not be necessary to explain the other drawbacks of textile fibres made from cellulose, they are very well known. The bad resistance to creasing, the weakening when wet are so well known that I shall not discuss matters here. All in all it must be said

¹ MARSH and WOOD, Introduction to the Chemistry of Cellulose, first edition, London (1938).

² FREY-WYSSLING, Die Stoffausscheidung bei Pflanzen, Berlin (1934).

³ G. P. 154 507, etc.

⁴ Cf. the review of L. ROSE, High tenacity rayon, J. Soc. Dyers Col. 61, 113 (1945).

that we have artificial textile fibres, but that they are far from being satisfactory or perfect.

The same is true for Acetate Silk which on the other hand is much more elastic. Acetate silk also has a very small molecular weight and cannot be compared with natural fibres with regards to physical properties.

It seems noteworthy that chemists have invented so many processes which depolymerise cellulose, and it seems to me one of the most difficult tasks to find out methods which will allow the production of cellulose fibres without diminishing the original molecular weight. We do not know whether it will be possible to build up from low molecular cellulose a molecule which will be larger, and the answer is in the future.

I may be permitted to discuss whether it is really necessary to produce artificial textile fibres from cellulose. There is enough cotton, linen, wool, and ramie available in the world to meet all the needs of man for textiles. At the same time I personally prefer a good popeline shirt to any artificial material, and I believe that this is the opinion of every person who is interested in the matter. So far cellulose textiles made from wood cellulose by the viscose process are only «Ersatz» whether we like it or not. Of course, we cannot stop the production of rayon at present, but we must face the fact that by devastating our forests by making paper and textiles from them we are responsible for the future.

We have seen during the last 30 years that dyestuff makers have started the so called *movement of fastness* with regards to dyes. It would be very interesting to see the effect if some firm started a similar movement of fastness with regards to physical resistance on the field of artificial textiles. Imagine what would happen if one could read in a shopwindow: "*Genuine English mercerised popeline. Degree of polymerisation 2200 guaranteed!*", and if one could read in the same shopwindow: "*Rayon, degree of polymerisation 420 guaranteed!*". I doubt if anybody would care even to look at the second item. Of course such ideas will not be very popular with the producers of the low polymeride, but nevertheless they are correct.

Things look a little different when we look at the recent progress made on the field of synthetic textiles. The first was of course Nylon which has outstanding properties. But at the same time this highly interesting material is no competitor for natural silk. Natural silk falls much more beautifully, it is warm and hygroscopic. Nylon is not hygroscopic and cold and at the same time, curiously enough, not fast to light. Nylon is the first attempt to replace a 1000 year old natural material but as far as one can see the attempt failed. In spite of its cheapness Nylon in its present form will not replace natural silk, which to-

day costs up to 60 shillings per yard and is nevertheless preferred to Nylon. Nylon is a product of its own and serves new purposes. Nylon stockings which weigh $\frac{4}{5}$ of an ounce a pair, do not prove the fitness of Nylon for underwear. Natural silk is a product which gave a living to millions of brave peasants in Italy and the far East. These people will not and cannot buy our goods if we refuse to buy theirs. Silk is related to agriculture, whilst Nylon is related to chemical works of great magnitude and industrial labour.

I do not discuss the newest development on the field of synthetic fibres. We know too little about Terylene as to be able to pronounce any judgement for the future. It is, however, my conviction that Nylon will soon be superseded by new products because CAROTHERS' discoveries are only now investigated in detail and he has left many questions to his followers to be answered.

Concluding the first part of my survey I should like to say that I believe that the only fact which will give a correct answer to the question of the *Value of Use* is the molecular weight. I believe that knowing the molecular weight of a given cellulose material we can say that its value of use is directly proportional to this *fundamental number*. No process, however elaborate, can change as a whole this value. I can give an instance which we have investigated in Zürich and St. Gallen: Whilst *tootalising increases the creasing value of a material* very much, on the other hand the value of *abrasion* is lowered nearly 85 %, that is to say the value of use is diminished.

The only treatment which improves a textile all round is still *Mercer's Process*. Mercerising is, however, a physical and no chemical process. Mercerising does not reduce the molecular weight but renders the fibre denser and more resistant. The other processes, also invented by MERCER as well as by F. SCHÖNBEIN, the *acid treatments* will give very beautiful effects, but they reduce the molecular weight and are not improving the mechanical properties at all.

These facts are known for about 20 years and they have given rise to some interesting improvements with regards to *bleaching*. The old and well known bleaching process with hypochlorite reduces the molecular weight by about 50 % and even more. The old bleaching on the lawn which is still used in France and also partly in Switzerland does not reduce the molecular weight. Linen or cotton bleached on the lawn is therefore much superior in use-value, a fact which was often doubted but which is quite correct.

There are two new processes which I shall only touch. The first one is the bleaching process where instead of hypochlorite chlorite is used. This process is excellent for it does scarcely affect the molecular weight of cotton or linen. On the other hand it is

at present too dear and it remains to be seen whether it will be possible to produce chlorite cheap enough.

The other process is the *du Pont Process* where hydrogen peroxyde and caustic soda is employed under pressure. We do not know yet whether this excellent process will replace the old one. In both processes the losses of material are very small, only about 2%. In any case we see that the natural fibres lend themselves still to marked improvements, and it is to be hoped that these processes will be successful.

Wool as one of the most important textiles has in fact no competitor, because the artificial imitations cannot be called real substitutes. They are in fact "Ersatz". On the other hand I do not see any necessity to try to make artificial wool at all. Sheep are very useful animals. They produce not only wool but also meat and hide from a soil which could not be used for agriculture. The casein fibres and all the numerous imitations are not interesting when compared with natural wool. The treatments of wool for different purposes are well known to the specialist. They have been developed principally in England. Chlorine was replaced by sulfuryl chloride or by elementary chlorine under various conditions. Wool when treated in such a way no longer gives felt and is ready for printing. The bleaching of wool is not interesting and is still effected with sulfur dioxide or hydrogen peroxyde. The reservation of wool to prevent its being dyed is a special feature which cannot be discussed at the moment.

The methods which have been developed for the protection of wool are well known. The new products such as the *Eulans* (I. G. Farbenindustrie) and the *Mitins* (Geigy) are well known to every textile chemist⁵.

I shall not speak of *Silk* because this would lead too far and things are well known to everybody.

Having dealt with some of the aspects of old and new fibres let us consider what is done with these materials.

The principles of dyeing and of finishing have not changed very much, but the different properties of old and new fibres called for changes, often very subtle but important nevertheless. We have seen that the chief difference of the old and the new fabrics lies in their different molecular weight, and this means that the new fibres are less resistant, especially when wet. We see therefore that the engineer tries to shorten the processes as much as possible not only on account of the cost of labour but more so because rayon and many other artificial textiles do not stand the old processes. It would be impossible to dye

rayon by the old Turkey Red process which 100 years ago lasted up to fourthnight. The material was illtreated to such an extent that, if rayon were taken, not much would be left. But even the more recent manipulations used for dyeing old fibres are too brutal for rayon, nylon, Bemberg-silk and all the other new textiles. Therefore we have seen very interesting changes during the last 30 years in modern machinery. Wooden apparatus have been mostly replaced by staybrite steels, at any rate on the continent and also in England. These apparatus are much smaller than the old dyeing machines and at the same time much easier to be cleaned. The concentration of the dyebaths is much higher than before, and this means that the dye and the chemicals go much quicker on the fibres, and easily produce uneven dyeing. This disadvantage had to be overcome by the use of new disperging chemicals, synthetic soaps and many other auxiliary materials which stand foremost in the interest of the dyers. In fact we have practically enough dyestuffs, and there is no urgent necessity to find new ones. Of course new dyes are made also to-day and they are quite useful but not very necessary.

Many of the old and once famous dyes have practically disappeared not because they were not good enough, but because they wanted too much time for application. The quicker a dyestuff can be applied the better for the fibre. Processes which attack the old fibres will attack the new ones still more. Thus we see that processes which at the first sight seem to be too expensive have been introduced because they are quick and do not damage the fibre. Even diazotation on the fibre is not popular with the dyer and many dyes which were formerly developed have only a small use to-day. On the other hand new dyestuffs of very great fastness have been developed. I may mention the *Fast Copper dyes* first produced by the German I. G. and the *Geigy Cuprophényl Colours*. These are dyed like a direct dyestuff and aftertreated with copper salts. The dyes thus produced are very often of extraordinary fastness to light and washing and equal to many more expensive vat dyes. I may also mention the *Indigosols* of MARCEL BADER. When these were invented the inventor had great difficulties to find a firm who would try the experiment. To-day the indigosols are amongst the best dyes we have, their application is very easy and their fastness excellent. The same holds good with the large group of the *Naphthol AS*. I remember very well how astonished we were in Basle when the first patents came out. The idea to use arylamids of 2-hydroxy-3-naphthoic acid seemed to us quite out of place, but we, as other people, were thoroughly mistaken. The *Naphthol AS* brands have in fact changed the whole aspect of cotton dyeing. On

⁵ LAEUGER, MARTIN, MÜLLER, *Helv. Chim. Acta* **27**, 892 (1944).

account of the facility with which these dyeings can be discharged and as we say "illuminated" (discharging and replacing the discharged colour by another colour) Alizarin and its analogues have practically disappeared. Similar products are the Neolan colours which give the shade wanted directly without after-chroming.

The necessity to quicken the dyeing process has led to many new suggestions, and we may be sure that in 50 years our dyeworks will operate on different lines. I shall only mention a very few of the new inventions because a complete enumeration would take too long. The dyeing of Viscose rayon yarn in cake form is not a fanciful idea but is based on the notion to treat the fabric as carefully as possible without damaging it⁶. The *E. I. du Pont de Nemours Co.* have elaborated a process for dyeing indigo at a speed which would have seemed impossible to our grandfathers. By using very finely dispersed indigo, and by simply padding the fabric in the presence of hydrosulfite or rongalite and caustic soda, cotton and other cellulose textiles may be dyed at a speed of over 200 yards per minute. The only question which I should like to ask is: Who is going to use this huge quantity of indigoblue cotton? Perhaps the Chinese, perhaps the Russians, at any rate not the four millions of Swiss who do not like to be uniformly clothed. This remark applies of course to every attempt to mass production, and this is not the place to discuss economics.

The fact that artificial dyes can be very quickly applicated and the other fact that artificial textiles behave differently from old ones has given rise to attempts to substitute dyeing through *printing*. Printing is the most interesting variation of making a textile coloured. It is as old as dyeing and perhaps even older. The trouble with ordinary printing is that it imitates only the dyeing process. Ordinary printing is local dyeing. This means that we have to use specific dyes for every material and at the same time take care that the print penetrates the fabric and is well fixed afterwards. It is easy to print every textile but the process is complicated. Printing should be cheaper than dyeing but as a rule it is not.

A way out has been found by some clever modifications of the very old pigment processes where albumine, caseine, and other fixing chemicals were used. Pigment prints rub off and they stiffen the fabric when used in the old way. The first inventor was, as far as I can make out, ZÜNDEL (Moskau) who as early as 1912⁷ proposed to fix pigments or any other dye with Bakelite. This process, however, has the great disadvantage that the whole of the thickening which is an artificial resin remains on the fabric rendering it very stiff. Whilst in the old processes

the thickening was washed off after the fixation in the case of ZÜNDEL'S process the whole of the mass remains on the cotton and cannot be eliminated.

The new inventions are based on the discovery made by PICKERING⁸, who showed that it is possible to prepare very stiff gellies by emulsifying two liquids which will not mix in the presence of a very finely divided solid which, on the other hand, is moistened by both liquids. It is curious that I was present at the reading of PICKERING'S Paper in Burlington House in 1907, and it seems strange that I should be permitted to speak here on this very subject 40 years later.

PICKERING showed gelly-cakes which were quite hard but yet contained only about 5 % or less solid matter, namely basic copper oxyde, and besides only water and paraffin oil.

Basing on this observation which, may be, was not even known to the modern inventors, new and highly interesting printing methods have been developed. The CIBA in their *Orema Print* produce pastes containing the pigment and chemicals which will fix the colouring matter when heated at about 140 ° C. The fixing materials are for instance casein, primary condensation products of phenol and formaldehyde, borax, and other preformed resins such as melamine and formaldehyde. These substances are mixed with water and toluene, paraffin oil, etc. They give a thickening stiff enough to be printed without any difficulty. On steaming the print the two or more liquids will evaporate leaving only the colouring matter and the fixing materials which combine with the fibre and the dye. By this method every pigment, and also dyes can be printed, and because the fixative forms only a minute quantity of the whole thickening the prints are soft and also very fast to rubbing much more so than the old pigment prints made with albumine.

A similar printing method is the *Aridye* process invented in the U.S.A.⁹ which has met with a great success as well as the *Sherday* process.

The new methods do away with the washing of the material after printing and thus do not damage it. I believe that the new tendency may go on in this direction and that the old dyeing methods will be superceeded, at any rate partially.

Summing up this rather shorthand paper I can make the following statements:

1. The old dyestuffs have still a wide range in their application, old dyes meaning those which have been invented from 1856 to 1920. Their application must be improved and we have enough good dyestuffs at hand. It seems more interesting to improve the dyeing methods than to find new dyestuffs.

⁶ C. M. WHITTAKER, *J. Dyers & Col.* **60**, 109 (1944).

⁷ Cf. G. P. 264 137, *Frdl.* **11**, 765.

⁸ *J. Chem. Soc.* **91**, 2001 (1907).

⁹ U. S. P. 2222581, etc.

2. The aim of the dyer is to quicken his processes not only for the old but also for the new fibres.

3. The artificial textiles will remain, but as long as their inner submicroscopical structure is so different from the natural ones they are no real substitutes for the old ones.

4. The aim must be to invent textiles which have at least as large a molecule as the natural ones.

5. The value of use is directly proportional to the molecular weight of the substances employed.

6. The new coming artificial textiles must be made from cellulose without diminishing the molecular weight because a low molecular weight cannot be changed by treating the finished product with any known process, such as tootalising and similar methods. The actual value of use remains in principle always the same.

7. New textiles should have an inner submicroscopical orientation similar to the natural fibres. Nylon is the first artificial textile leading in this direction. I consider Nylon only as the beginning of a quite new era of modern textile chemistry. Finally I should like to say that parallel with the development of new artificial textiles the modern auxiliary

products should be improved. At present there seem to exist too many of them. A new tendency to go on different lines is already noticeable in the U.S.A. where artificial soaps are produced on a very large scale using petroleum as a starting material. I did not enter into this field but I should only like to say that here new improvements are to be expected.

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