

must take up the whole of the differences between the forces.

$$R_1, R_2, R_3, R_4, \dots, R_n,$$

$$\text{and } R_1', R_2', R_2', R_4', \dots, R_n',$$

Now since

$$R_n - R_{(n-1)} = P \left[\frac{1}{\cos \alpha_n} - \frac{1}{\cos \alpha_{(n-1)}} \right]$$

and

$$R'_{(n-1)} - R'_n = Q \left[\frac{1}{\cos \alpha'_{(n-1)}} - \frac{1}{\cos \alpha'_n} \right]$$

therefore a greater rise or fall not only of the rows of force R and R' , but also of the angle rows α and α' corresponds to a greater friction.

That is to say, if an increase of the coefficient of friction between warp and weft makes the curves of Figure 7 steeper, its reduction flattens them.

The point N and with it the α_g curve could be *raised*, for instance, if the friction of the threads during *beating up* could be *made less* than during the return of the sley, for then the curve LN would be made flatter than shown in Figure 7, but MN , on the contrary, steeper. There are as yet no means of doing this at disposal.

It is quite practical, however, to raise the point M and with it the whole of the curve which starts there (curve M' , N' , Figure 7), whereby a new much higher point N' , and thus a higher α_g line are produced. This measure therefore proceeds from an enlargement of the angle α_1 , that is to say, it is found in practice in the shape of a soon shed.

The shedding motion here works so that the *next shed* is already almost opened at the moment when the sley beats up. From the foregoing it will be evident why this method of shedding is so much used just for the plain weave.

The best means, however, of influencing the final weave angle is to be found in point L . When it is raised to L^II , that is to say, through an enlargement of the angle α' , the angle α_g^II is much greater than α_g . A subsidiary result of this procedure, however, is that the zone of the fabric affected by beating up becomes greater, the limit N^II moving towards the breast beam. The use of the soon shed has besides the *contrary* effect (Figure 7).

The angle α_1' can *practically* be enlarged in the following way.

First of all the *forward movement* of looms with the usual positive clothbeam mechanism is made smaller, so that *less cloth* is pulled forward from pick to pick. It is, however, not certain whether this measure *alone* is suffi-

cient. Of course the reed at the moment when it beats up can now press the new weft thread *further* into the fell of the cloth than before, whereby at first, it is true, the angle α_1' is enlarged as desired, but it must not be forgotten that as α_1' increases a *continually greater share* of the tension arising from the warp let off motion is *directly transferred to the reed* through the new pick, as can be seen from Figure 6.

In this way the active pulling force ΣQ still remaining in the fabric can be so far reduced that it no longer suffices to disturb the weft which has already been beaten up. Then, however, the enlargement of α_1' cannot lead to an enlargement of α_2' , α_3' , etc., nor can α_g for the present be raised further. This condition is known as the *forecloth limit*.

If the angle α_1' is enlarged still further by again setting the regulator still smaller, then the forecloth is actually produced, that is to say, the fabric between the fell of the cloth, the breast beam, and the cloth beam *loses all tension* when the sley beats up. The closeness of the weft is not raised in the least as compared with that reached at the forecloth limit. Thus more fabric is woven than the cloth beam takes up, and the length of the goods before the breast beam continually grows further into the path of the beat up. The reed touches the fell of the fabric more and more before the dead point and leaves it later and later. The whole of the warp during the beating up is plucked hither and thither by the distance to which the cloth has grown into the path of the sley, whilst the warp beam is being vigorously rolled and jerked to and fro. No warp will stand treatment like that for long.

To sum up. In order to make the weft closer, it suffices to increase the angle α_1' by setting the regulator lower only until the forecloth limit is reached. Beyond this limit an enlargement of α_1' is only effective when at the same time the *rest tension* ΣQ is kept sufficiently high, *by increasing the tension arising from the warp let off motion, that is to say, for example, by raising the drag weight*.

It can now be supposed for a given material for warp and weft that the proportion $\Sigma Q : \Sigma P$ is definitely settled by the size of the angle α_1' . If this proportion is zero, then raising the drag weight will have no effect. The *actual* forecloth limit must therefore really be much lower, at a point already where the proportion $\Sigma Q : \Sigma P$ is still finite. It is



evidently to be found at the point where the *absolute value* of ΣQ is compensated by the *bending strength of the material used for the warp*.

This bending strength strives at least to flatten the undulating curves of the bending line of the warp, since it is not elastic enough to stretch it completely, as can be seen from the form of a thread taken from a sample of cloth. This flattening tendency produces *pressure strains* in the intersecting cross-sections A—B, C—D, E—F, and so on which are in themselves extraordinarily low, but which are able to negative a very weak Q tension. By strengthening ΣP , however, ΣQ will rise in the same proportion and in this way it is possible to give the low pulling tension a preponderance over the low pressure tension again.

The effect of the *bending strength* solves at least temporarily the question as to the action of the *brittleness* of the material on the attainable closeness of the weft, for it tends to reduce the friction of the warp upon the weft, its effect being greater, the smaller the pulling forces are that act in the direction of the warp. Consequently the bending strength will exert a *more flattening* effect on the curve MN in Figure 7 than on LN and therefore lower the point N and with it α_g a little, and that the more for the same reason the smaller ΣQ is, that is to say also ΣP . *Just for this reason artificial silk which is of extreme bending strength reacts so sensitively to the drag weight, that is to say, to the tension which proceeds from the back rest regulator of the warp let off motion.*

The alternating play of forces of the weave is not without its effect upon the position of the *warp threads* in relation to one another also. In the first place, the transverse tension $Z = N \cdot \cotg \beta$ mentioned above strives to pull the warp threads together. Besides this, forces may appear which try to equalize any inequalities in the spacing of the warp threads, such as can readily occur when the reed wires are comparatively thicker than the warp threads. This tends to produce irregularities in the weave angle of the weft also and then differential forces appear corresponding to the forces D_r in Figure 5 which tend to push the warp threads towards the smaller weave angle of the weft.

Complete equalization can never occur, because the *friction* between warp and weft stops the lateral movement of the warp

threads even before they have adjusted themselves to the same distance from one another; consequently the *reed marks* make themselves noticeable and the cloth is reedy.

When weaving smooth yarns, such as silk and artificial silk, the position of the warp threads can be improved by an aftertreatment of the cloth (cross-brushing). Rougher yarns, in particular cotton and wool, require an arrangement for use during the weaving to equalize the spacing of the warp threads.

This is already done to a certain extent by arranging the shafts so that the middle of the shed lies below the tangential plane of the breast beam and the back rest. Then in shedding the threads of the lower shed absorb much the greater part of the tension of the warp, while the upper shed is just taut enough to permit of the shuttle passing through easily. Thus at each change of shed most of the tension of the warp is transferred from one half of the warp threads to the other. This tends to produce continual shocks and disturbances of equilibrium in the newly formed fabric which are often strong enough to negative the resistance offered by the friction and thus to remove the reed marks. If the yarn is *very rough*, however, the action of the "loom fulling" to be effective must be enhanced by a *positive motion of the lease rods*, which thus act as rocking beams.

The rocking beams move in the same way, swinging up and down so that alternately one half of the warp threads absorbs the greater part of the tension of the warp and the other half the smaller part. Now if the warp is drawn in *two threads* through the rods, i. e. in such a way that each two adjacent threads run in the same direction through the lease rods and weaving is done at the same time with a *loose warp*, then Figure 9 shows the situation at *each* shedding.

One-fourth of all the warp threads (a in Figure 9) has a very high tension which is due to their position in the lower shed together with the rise of tension caused by the rocking beams. Two other fourths (b and c in Figure 9) are under a lower tension because either the strain in the lower shed is equalized by a lowering of the tension in the rocking beams, or the strain in the upper shed by raising the tension. The remaining fourth of the warp threads (d in Figure 9) is tensioned very weakly because the strain in the upper shed coincides with a very weak pull in the rocking beams. The order in which the four degrees of tension are distributed among the four

groups of warp threads changes with each change of shed, as is shown by Figure 10.

The higher or lower tension of each warp thread now affects the ends which have already been woven in by causing them to set



Fig. 9

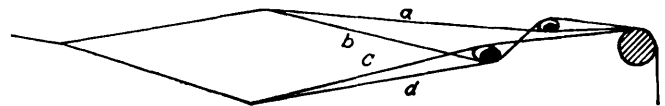


Fig. 10

a greater resistance to the compulsion to undulate, the higher the tension they are under. Thus in the strip of fabric between the fell of the cloth and the breast beam, warp threads alternate with quite different degrees of undulation. Since further each pick must cross

materials may even be so rough that the differences of the weft weave angle caused solely by the irregular spacing between the warp threads cannot afford compensation. Figure 12 shows the same fabric (the area between fell and breast beam) under tension in the loom, weaving being done loosely with the lease rods in action. It can be seen how the different bending through of the warp threads has so enlarged the small differences of the weft weave angle that the friction of the material can be overcome and the reediness of the finished cloth disappears. Figure 13 again shows the same fabric after the change of shed, and it is evident from it that the corrections for distance which have not been able to be done in the one form of shed most certainly take place after the change of shed.

The lettering of the warp threads is the same as in Figures 9 and 10, that is, Figure 12



Fig. 11

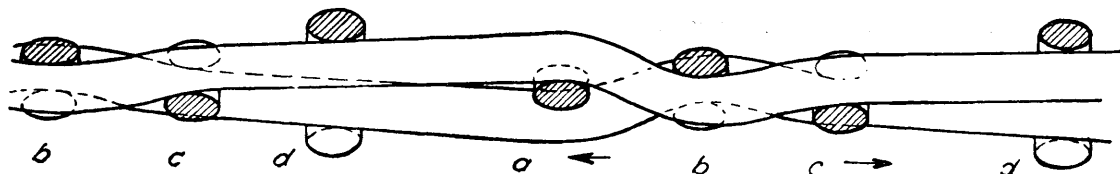


Fig. 12

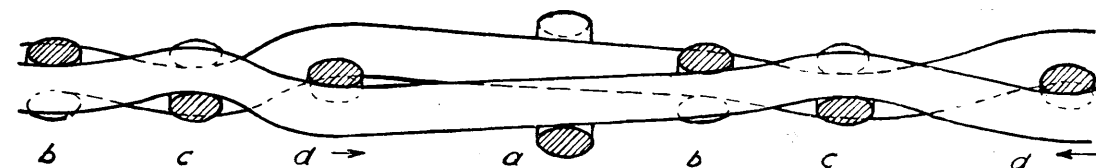


Fig. 13

all the warp threads, an artificial, so to speak, periodic irregularity of the weft weave angle is produced throughout the whole of the fabric.

Upon this is based the action of the rocking action upon the distribution of the warp threads. Figure 11 shows a cross-section of the warp of a fabric every three threads of which are reeded through a very coarse reed and therefore is strongly reed marked. The

corresponds in the position of the shed to Figure 9, and Figure 13 to Figure 10.

When the cloth is taken from the loom, all strains disappear from it which are due to the action of the tension of the warp let off motion and the braking action of the weft. On the other hand, all those strains become conspicuous which owe their origin to the last remains of the elasticity of the material woven, and strive partly to flatten the un-

dulating curves of the threads, partly also to strengthen again the outline of the undulations; in particular the tendency of the threads which have been pressed flat partly to recover their original cross-section acts in this direction and is the cause, among other effects, of the shrinkage in length of the finished plain woven cloth. This effect must be considered as taking place in the following way. The weft swells up and compels the warp, which is now freed from the tension of the beam, to assume a strongly undulating form again, while the fabric shrinks only slightly in the width.

After cloths woven heavily *twisted* yarn have been removed from the loom, forces are freed which *tend to reverse* the twist and which, especially if they are supported by a wet chemical aftertreatment, exert a powerful influence on the position of warp and weft, and produce the *crepe effects* nowadays so much admired. If a number of short sections of the weft are afterwards drawn together, this disturbs considerably the inner equilibrium of the finished plain woven cloth.

It occurs under certain conditions in silk and artificial silk articles and gives them a crumpled or crinkled appearance. On the other hand, it will seldom be found that plain woven cloth curls as, for instance, sateen woven fabrics often do after having been stored for a long time. Since all the ends and the picks are equally distributed on *both sides* of the cloth, all strains also are equally distributed on both sides, and there is no strain present which could cause curling.

One other point fundamentally distinguishes the plain weave from the sateen weave and that is that neither warp nor weft has an opportunity of forming a cover either on the face or on the back of the cloth. They cannot cover each other and consequently there is no cloth in which all weaving mistakes appear with such terrible distinctness as in the plain weave. And that is one reason more why the weaving of a perfect plain woven cloth, of whatever material, has always been considered as *the* masterpiece, redounding to the credit of weaver, overseer, and designer alike, no less than of the preparation and finishing.

The Curling of the Selvages in Fulling

By *A. Farmer*, Weaving Mill Manager

It is well known that this nuisance has often led to differences of opinion between weaver and fuller, so that it would seem that a few remarks upon the subject are called for.

Curling of the selvages in fulling occurs chiefly in goods which are not woven alike on both sides, one being weft and the other warp, like twill, cross twill, sateen, and so on. The curling takes place towards that side upon which the weft floats, whether that is the face of the cloth or the back, and is due to the greater inclination of the floating weft to crumple. This is particularly the case when the milling machine is so adjusted that the goods pass through the trough without the beating mechanism being in action, the goods being thereby fullered more in the width than in the length. The curling of the selvages happens very quickly, according to the adjustment, and it does not take long before the fabric has rolled together like a roll of paper. It is not of much use to open out the piece or stroke down the curled selvages with the thumb, for the goods in a short time are in the same state again as they were. The next thing that happens is that the fabric is less

felted along the selvages because they are always inside and are hardly worked over by the cylinder. This drawback, which can almost drive a fuller to despair before the goods have been finished, can be met in only one way, and that is by weaving the selvages in a different way from the fabric itself, making the weave the same on both sides.

The plain weave and its derivatives here come into consideration, Figures 1, 2, 3 and 4. If the weave of the ground does not require too much weft, that is if the plain weave of the selvage causes no trouble, the weave shown in Figure 1 is sufficient, but if trouble is caused then the weave of Figure 2 or 3 must be adopted. The weave of Figure 2 always requires two picks in a shed and they lie close together. In the weave of Figure 3 one pick falls in each shed, the selvage threads, however, always have the same position in pairs and the picks lie comfortably beside one another. The weave of Figure 4 takes up even more weft and is especially suited for selvages with backing weft. The weave of Figure 5 can be used in place of that of Figure 2 or 3 as conditions require. In fabrics in which the same number of ends always

form upper shed or lower shed the selvages can be allowed to work in the harness, for they will not curl. This applies also to double cloths in which the upper and the lower warp always work equally.

It is further advisable, especially when the

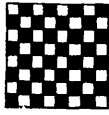


Fig. 1

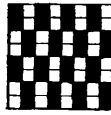


Fig. 2.

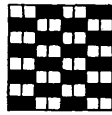


Fig. 3

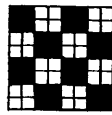


Fig. 4.

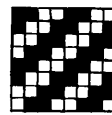


Fig. 5

cloth is a sateen weave, to try to keep the selvages no thinner than the fabric itself. A thicker selvage has been found to curl less than a thin one.

Goods which do not have a suitably woven selvage and consequently curl readily during fulling must be well opened out during the operation more often than is usually done.

For instance, if the throat before the entry channel has been considerably worn away or the entry channel itself is worn, then the goods are much more inclined to curl.

One good way of preventing the goods from curling is to double the piece as a bag, with the face inside, and stitch the lists flat together with twine. Then curling cannot happen at all, however the selvages may be. If there is too much air in the goods thus sewn together, the seam must be opened a little to let the air escape.

The selvages of goods which are fulling by the more or less severe action of the beating mechanism do not curl, even if the goods are one-sided, but they fold over as a rule so that they partly lie double. It is therefore advisable always to use one of the weaves mentioned above so as to be definitely certain of not meeting with the drawback.

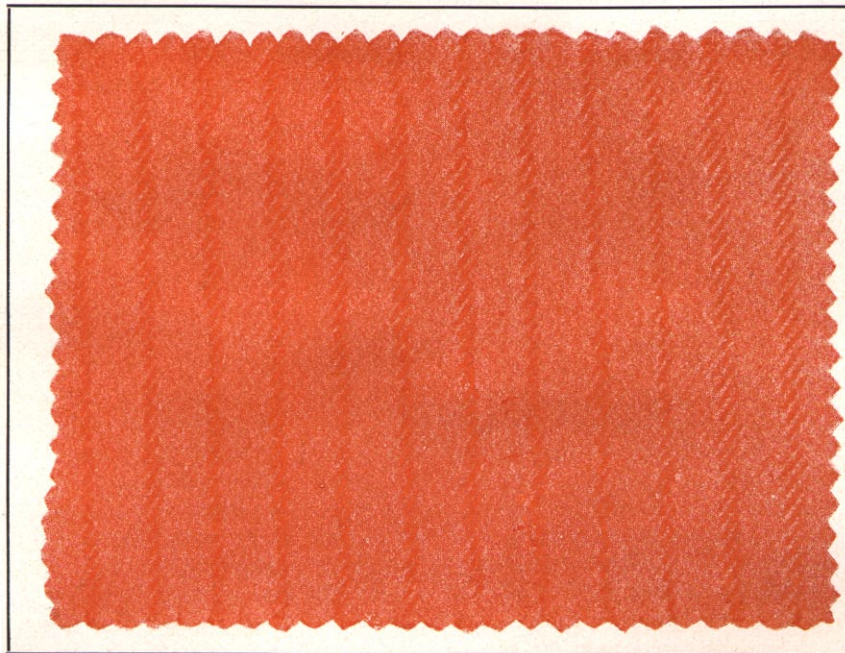
Producing Raised Effects in Stripes on Fabrics*)

By *E. Wenzel*

The raising machine shown in the accompanying illustrations is a novel finishing machine, by means of which longitudinal and

been raised, without the use of stencils, or the like.

The novel effect is obtained by employing



wavy striped effects can be produced on ordinary fabrics or on cloth which has previously

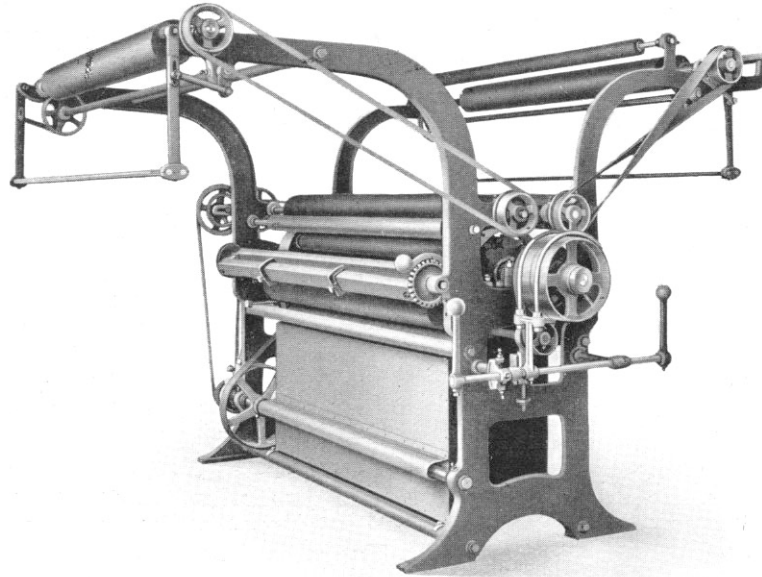
differently fluted raising rollers and the width of the stripes can be varied simply by changing the position of each pair of rollers to each

*) Messrs. Ernst Gessner, A.-G., Aue i. Erzgeb.

other in any pattern desired. The novel and striking results produced on a single-shade or multicoloured ground are likely to arouse general interest and are capable of much variation. The effect can be heightened by

ly in a single run, a special change of speed for the cloth is provided which permits of speeds of from 0.5 to 1.5 metre per minute.

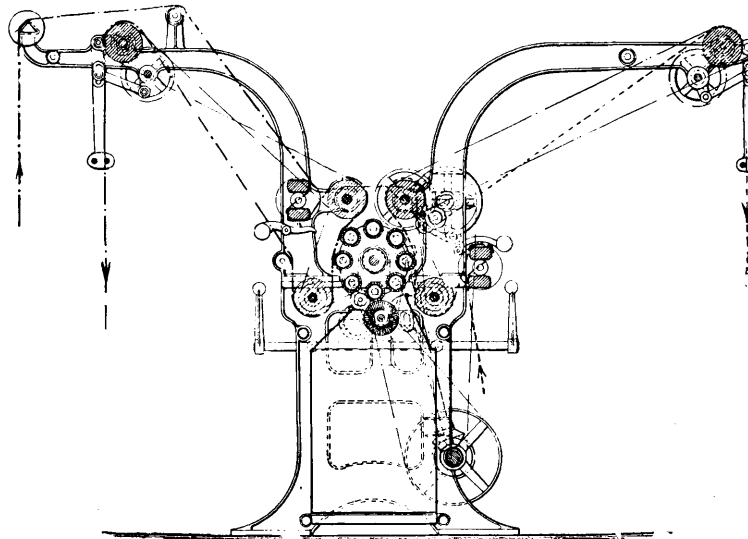
The original raising machine is furnished with two double tension bars, guide rollers,



printing stripes with one or more colours, or by previously raising the ground.

The machine can be used for felting by exchanging the rollers fitted with raising rings

and cutting appliances which act quite separately. Consequently two widths, or four half widths, can be handled simultaneously whereby the output is much increased.



for completely clothed rollers and a complete wrapping of the cloth on the main cylinder. In order to raise stripes thoroughly and dense-

Finally we would mention that the machine is furnished with a clearing brush and dust collector like the ordinary raising gig.

Which is the Right Side of a Fabric?

By F. Schweiger, Managing Director

Whoever has to do with textile fabrics has to face this question practically every day. Years of practice and a fine judgment are, generally speaking, the most important guides, but any such judgment only carries conviction when it can be proved.

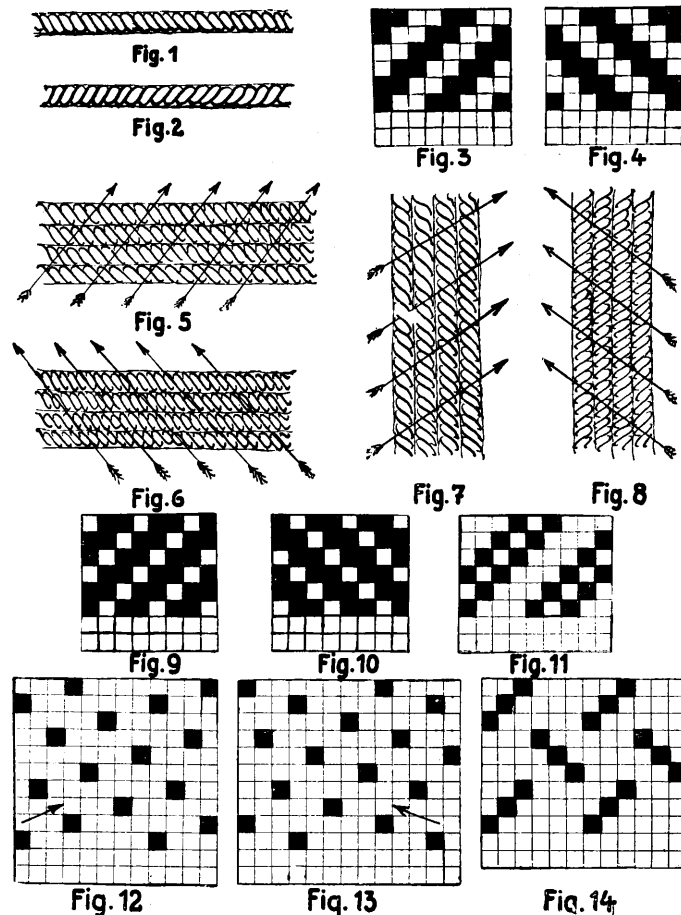
The right side of a cloth is, as a rule, that surface which has a superior appearance to the other side. The one surface is sometimes called the side with the good pattern, and the other side that with the inferior pattern. This indicates that that side is viewed as the upper side which is better in appearance, that is to say has better material, is better finished and is thus more impervious to external influences. These general characteristics are to be found in woollen goods, in raised goods, in velvet, and so on; smooth articles, however, which are two-sided, that is to say, the two sides of which show the same, or, rather, practically the same characteristics, for instance, linen, double twill, twill the same on both sides, etc. offer considerably more difficulty.

Every expert is aware that a mathematical sameness on both sides in nowhere to be found. Neither nature nor art can produce such an article. The same principle applies to fabrics, so that the manufacturer supplies all his products with two different sides, one of which is called the right side of the cloth and the other the back of the cloth.

In most cases attempts are made to find the right side by comparison, laying both sides of the cloth, for this purpose, beside one another. The face of the cloth has the more agreeable appearance, it is better finished, the lay of the wool is smoother, the fibres are arranged regularly and are more uniform in length. This can be particularly well observed, if the cloth has been sheared or singed, by holding it against the light. Shirtings and dress goods, on the other hand, have often the same finish on both sides and it is then necessary to understand something

of the technique of the art in order to come to a judgment.

It should first of all be mentioned that the threads which go to make up the fabrics are composed of single fibres which hold together by having been twisted. For practical reasons based upon the nature of the fibres single yarn is twisted as shown in Figure 1, while



doubled yarns composed of such single yarns are best twisted together in the opposite direction, Figure 2. If special value is attached to the twill line in a twill fabric, it must show up well on the surface of the cloth and look fresh even if the goods have been stored for some time. Figure 3 shows a Cashmere twill with the line running to the right, and Figure 4 a similar cloth with the line running to the left. If the goods have weft effects and

single yarn, as is generally the case with dress goods, the direction of the twill line will be prominent when it runs to the right, as shown by the arrow in Figure 5, but it will be indistinct when the line runs to the left as indicated by the arrow in Figure 6, that is to say, when the twill of Figure 4 is taken.

The fabric shown in Figure 5 is therefore considered to be the better and more agreeable in appearance, while that of Figure 6 is less appreciated if the surface of the cloth should be smooth. But if it is a woollen fabric or has a rough surface which does not show the twill and the twill line so prominently, then the cloth of Figure 6 will be considered the better and that of Figure 5 the less suitable quality for wear.

If a doubled warp produces the chief effect in the cloth, so that the surface is mainly warp which lies as shown in Figure 7, then the twill line must run to the right, that is, Figure 3 must be accepted as the face of the cloth. A fabric with doubled yarn in the warp and a twill weave will look better as shown in Figure 9 than in Figure 10 when the yarn twist of Figure 7 forms the face of the cloth, but the better cloth must have the twill line of Figure 10 when the warp yarn is twisted as shown in Figure 8.

In the same way cloth which has been woven as shown in Figure 11 looks better

when the weft, which is generally twisted as shown in Figure 1, runs in the opposite way to the twill line of the weave. This applies to all smooth fabrics which have not been raised, such as linings, serge, and so on, but it is more advantageous when the weave line and the twist line of rough or woollen goods coincide.

Further it is not a matter of indifference whether the sateen weave of Figure 12 is taken or that of Figure 13 for a cloth with weft effect. If attention is paid to the direction of the arrows and the order of the picks, it will soon be seen that the one sateen weave has a more agreeable effect and that the other is inferior, according to the way the yarn has been twisted.

Figure 14 shows a weave without a twill line. The roughened effect plays the chief part in such goods and in this case it is advisable to choose the goods with the best staple and clearest in appearance.

It will be seen from the foregoing remarks that the instructions given in various books on the subject to choose the twill line in the direction in which the German letter "i" is written, that is to say, obliquely slanting to the right, are only conditionally correct. The face of a cloth always depends upon the nature of the material and the finish. A little practice will often be of great value here.

Modern Points of View in the Construction of Textile Machinery

By *Conr. J. Centmaier*, Consulting Engineer

Textile machinery being part of the large group of works machinery is governed in its construction by the same technical and economical laws that apply to the group. But textile machines differ from other works machinery, especially from the machinery used for metal-working, in many very important respects. These differences are due to the nature of their field of application and to the raw materials which textile machinery has to work with.

Textile raw materials, both partially and completely worked up, which are subjected to the various processes of textile machines, are characterized by the relatively small size of their constituents, by low strength, both absolutely and relatively, by an elasticity not met with in other materials, and above all by the fact that they are very readily affected by external influences, such as atmospheric

humidity, the temperature of their surroundings, their content of static electricity, and so on.

Since textile materials, whether raw or processed, are very readily affected by external influences, the working parts of textile machinery demand a much more rigorous observation of their basic principles and must be much more carefully adapted to the use to which the machines are to be put than is the case with other classes of machinery. For a long time, therefore, the construction of textile machines has been removed from the realm of empiricism and plays an important part in the science of working machinery, although indeed many textile machines are still built according to figures and rules that are purely empiric. The scientific treatment of the principles of the construction of textile machinery is in spite of this still in its

infancy, just as the whole of our mechanical technology is still very far from being able to represent itself as a mature science. There is here wanting a generally applicable explanation of the various physical phenomena which go to form the nature and the characteristics of the construction and working of mechanical constructions. For instance we have not yet arrived at any generally accepted explanation of the theory of mechanical power.

Both verbally and in writing as well as in connection with explanations of the nature of electricity the author has since about 1916 given an explanation of the phenomena of mechanical power. He regards these as infinitely small vector whirling motions of the smallest particles of matter which in their totality form the macrocosmic phenomena which we can appreciate with our senses and our instruments. These explanations have proved themselves to be extremely fruitful for the understanding of all physical occurrences and will doubtless before long become common property in the science of physics, since they have proved that they can elucidate also all border phenomena. It has hereby been found that all physical forces, such as gravity, light, electricity, heat, chemical forces, and so on, are merely different aspects of one and the same original force. They are all subject to the same universal forces, whereby they influence one another, and the same laws, which are thus universal, always apply.

The most important fact for our present survey here shows itself with compelling lucidity. It is seen that the inertia of material mass particles is based upon the rotation of the vector whirling motion of the smallest particles of matter and that therefore the dynamic conditions in the construction of work machines are much more important than has hitherto been expressed in the practice of machinery building. This fundamental fact has most regrettably been neglected especially in the building of textile machinery, and to this is due the unsatisfactory constructions often encountered and their even more often unsatisfactory action both technically and economically.

We shall now consider in due order the raw materials for the construction of textile machinery, their construction and action from a modern point of view in reference to the most suitable construction and action technically and economically that can be attained. The space at disposal naturally permits of a

treatment of the most important points only, but apart from this the present study makes no claim to treat fully and finally all the important modern points of view which appear in presentday constructions.

Cast-iron is one of the most important materials used in building textile machines. Thanks to refinements in the scientific and technical methods of research it has been possible to work out an efficient technique for smelting and casting all kinds of cast-iron quite independently of the various types of ore. The quality and uniformity have at the same time been raised and especially the strength of cast-iron prepared under strict chemical and technical control has been greatly perfected. Special raw iron from England is no longer used so much as it was after it had been found that the English cold-air iron could with advantage be replaced by careful mixture of good waste iron, such as steel and cast-iron chips or shavings. Cast-iron that is intended for vessels which have to work under high pressure is at present preferably made with the addition of manganese, and ferrosilicium is also used for this purpose.

Charcoal-iron possesses excellent properties due to the slight content of carbon and the absence of phosphorus and sulphur, as also the analogous silver-iron. The McLain process is much used in America for cast-iron for the construction of textile machinery because the content of silicon and especially of manganese is high. The original Martin process which produced steel by smelting waste steel and raw iron together has been extended in the last few decades by the use of pure chips using retort coal, carburit, etc. as the carbon carrier. Now that the electric smelting furnace has succeeded in preparing the so called synthetic cast-iron, it is probably destined to bring about an important improvement in all classes of foundry technique. The strength of cast-steel can be improved at only a slight extra cost. Malleable cast-iron, which many firms make themselves, is much used in the construction of textile machinery. American malleable cast-iron, characterized by its fracture showing a black core, should be a valuable addition to our foundries since it shows much increased extensibility and specific energy of shock. The types of steel which the presentday constructor of textile machinery has at his disposal may be grouped as follows: crucible steel, electro-steel (acid and basic), Siemensmartin steel (also acid and basic), Bessemer steel, and Thomas steel.

The uses to which these kinds of steel are put are determined by the nature of the qualities which are required of the various textile machines. The question whether in a given case cast-steel should be used instead of cast-iron must be decided by the strain which the machine has to stand and the saving in weight. In spite of the higher first cost, cast-steel will very often be found to be cheaper. As is well known cast-steel can also be forged and this quality can often be taken advantage of in the construction of textile machinery. Special kinds of steel produced by the addition of nickel-chromium, manganese, partly together with silicon etc., are of more or less importance for textile machinery, and very valuable case-hardened rollers, castings unaffected by acid, and so on, can be made by the use of such additions. Brass alloys with the addition of iron and aluminium have recently been tried out in foundries with success, and Bab-bitt metal for bearings has been created by the combination of lead, antimony and a little tin. Alloys with the addition of calcium and barium are also used nowadays. Monel metal, an aluminium alloy, has become of considerable importance for the construction of textile machinery abroad. Cast-aluminium with certain additions can be used to advantage for textile machines intended for export. Besides its low specific weight, this material has the further advantage of being a good conductor of heat, so that its use is to be recommended for equipment for equalizing heat, cooling apparatus, etc. Aluminium alloys can be made with the addition of copper, zinc, silicon, carbon, iron, phosphorus, manganese, lead, etc. and then possess specific properties, such as great hardness, good heat conductivity, not being affected by chemical action, and so on. Aluminium and its alloys can be looked on as the metal of the future for textile machinery and a general economical interest calls for every effort being made to develop the use of this material since it can replace other expensive metals which have to be imported from abroad, such as copper, with success. Its electrical conductivity is also comparatively good, so that it is excellently adapted for certain textile electrotechnical apparatus which are continually coming more into favour. Now that the nature of corrosion phenomena has been better comprehended and effective steps have been taken to combat it, brass has recently found more extended use in the textile industry, particularly for equipment which makes use of some chemical-

technical principle or other. Brass piping is now being used more and more in America for water pipes after it had been found that material which was extremely well adapted for this purpose could be obtained by properly mixing the constituents and treating them suitably both thermally and mechanically. It should finally be mentioned that Krupp's "soft iron" is suited for many purposes in the construction of textile machinery instead of copper. It contains about 0.06% carbon and about from 0.12 to 0.14% manganese and is extraordinarily soft and tough both when heated (to about 200° C) and in the cold. Its strength at from 18° to 200° C is about 3200 to 4400 kilos per square centimetre.

Referring to the process for the production of cast-iron the spray casting process should also be mentioned. Its use is continually extending and it is applicable not only to pure metals, but just as well to alloys. For instance alloys with tin and lead, and then with zinc as basic material can be recommended for the construction of apparatus, as well as zinc alloys with the addition of copper and aluminium (Spandau alloy). Durolith metal is very strong and shows a strength of 30 kilos per square millimetre.

Foundry technique has reached a high pitch by the development of casting machines, and the use of an endless transport arrangement alongside form machines set up in a row for continuous working has recently been introduced in this country. Another novelty is the shaking casting machine which is much in vogue in America. Foundry technique has further been enriched by the clay casting process which avoids the use of a pattern, but makes high demands upon the skill of the technicians and workmen. If a skilled foreman watches the form carefully he can always make a success of the process. It is of course of the highest importance economically because it dispenses with all overhead costs for the preparation and storage of patterns.

It is fitting to close the above survey of the metals with a few observations upon the most important methods for testing metals as to their suitability for machinery construction. Recent investigations have shown that the ball pressure process, at any rate within the limits set by the technique, is quite as valuable as the static process as carried out according to Brinell's method. Also the notch shock test has found an important explanation through recent investigations. Important theoretical researches, full of significance for

practical work, have been carried out upon the tensile bending test and especially upon the torsional stress of constructional parts. The well known formula of St. Venant has been expanded or partly supplanted by Föppl, Weber, and others. Euler's lateral flexure formula, which has lost much support since the collapse of the gasometer in Hamburg, has been successfully replaced by new formulae, in particular by that of Tetmeyer. Important investigations have also been published upon the bending of plates of varying thickness both singly and superposed, the results of which are of great significance for the construction of textile equipment, because just in this connection calculations were more or less empiric. The suitability of other materials used in the construction of textile machinery, such as wood, leather, fibre, have been further cleared up by valuable researches, and they can now be chosen very reliably for the most various purposes.

In recent years also the static and dynamic conditions which as a rule are of the highest importance for the construction and working of textile machinery have also been the subject of interesting and fruitful investigations. It is the bounden duty of every textile technical school nowadays which aims at imparting to the constructor of textile machinery rather more knowledge than usual of the nature of textile machines to pay more attention to applied kinematics and not merely to the arithmetical side of the science, but in particular to the problems of designing.

The author has more than once proposed to make dynamics the most important subject at higher schools and to treat statics as a special case of dynamics. Technicians of all ranks at the present day are face to face with dynamic problems without, as a rule, having the necessary equipment to solve them, because the necessary methods of treatment have not been imparted to them. Besides this it is a fact that power machines are generally treated rather broadly at the technical schools, so that little time remains for the statical and in particular for the dynamical problems. That is to say, it is considered sufficient to treat of the conditions relating to speed and strength in textile machines, but the problems of mass action, the forces of inertia, the phenomena of vibration, the forces of acceleration are, as rule, not gone into at all thoroughly. If these questions are explained and treated with the aid of diagrams, even not very skilled people can imbibe sufficient knowledge

of kinematic laws and phenomena with little trouble, because this field of theoretical technics is particularly well adapted for treatment by this method. It must further be borne in mind that a great many conditions obtain in the construction of textile machinery which, far from being completely explained statically or dynamically, have not even been sufficiently investigated. This affords an excellent opportunity to a young textile technician or engineer for independent research and his labours in this field would be well rewarded. Besides this no great expense would be involved, because expensive experiments are not necessary. The following tabulation of the various drives of a general nature which serve to transmit motion will show the problems that await attack here:

- a) for (preferably) uniform or irregular movements — spur gear, bevel gear, hyperbolic gear, worm gear, and so on;
- b) for irregular movements — not round wheels, elliptic wheels, eccentric circle wheels, chains with and without cam and crank movement, pulley guide motions, eccentric crank mechanism, guide link motions, roller levers, etc.

All the systems of motion mechanism enumerated are to be found in the construction of textile machinery and can often be applied for new constructions with great advantage if their static and dynamic characteristics are well enough known. It is of the highest importance in building textile machines to pay attention to the static and dynamic laws which come into question, if constructions are to be attained which are technically irreproachable and especially economically suitable. Although the static forces as a rule are sufficiently considered in the calculations of strength and the determination of the speed conditions, the dynamic conditions are very far from being paid proper attention to. The noise of many textile machines, the oft-recurring breakages, occurrences which often remain unexplained, and the great waste of constructional material often met with could certainly be avoided if the magnitude and direction of the forces that here make their appearance were properly cleared up. To cite merely one case, the use of weights is very unsuited for mechanisms which must move rapidly, because the forces of inertia inseparably connected with the weights oppose powerful forces of acceleration to rapid motions. If, however, springs are used instead of weights, the forces of inertia are practi-

cally zero. Another instance concerns the loud noise which often accompanies the action of textile machines, such as looms, beaters, etc. The energy of vibration of the particles of air which produce the noise must naturally owe their origin to a source of energy. This proves to be the mechanical phenomena at the parts working which can be shown to be deformations and cause not merely a loss of heat, but also produce great loss by radiating free energy in the form of vibrations. If these can be suppressed, the sound waves cease and the consumption of power can be reduced.

It is an extremely important task for every builder of textile machinery to endeavour to find a cause for the often inexplicable fractures which occur. He must first endeavour to understand accurately and definitely the static and dynamic forces which make their appearance. If this principle applies to the improvement of existing machinery, it is still more applicable to the creation of new machines, although the conditions often are much more difficult here.

Of course the technological conditions which govern the nature, the measurements, the speed, the power, etc. of the construction of the textile machine in question are fully as important as the purely mechanical conditions which come into consideration and determine the construction. All phases of the physical operating conditions upon which the textile technological process is based must naturally be thoroughly known. Unfortunately there still remains much to be done in this direction in the textile industry. The practical operation of most textile machines and the conditions under which they are technically and economically successful are, it is true, well known, but there is often no clear comprehension of the important physical phenomena. The result is often that a state of affairs arises, when the operating conditions have to be changed, which causes difficulties that are hard to avoid. Even in new constructions it often happens that there is no guarantee of final success and satisfactory operation is, in fact, often reached after expensive trials.

In the construction of new textile machines the results of textile research, so far as applicable, will naturally be made use of, if need be first of all by trial to create the missing scientific basis. The present state of the art permits of saying definitely in advance how a new mechanism will act, but mistakes should be strictly avoided in view of the economic

position of every business. It is further of great importance at the present time to pay attention to the physiological, partly also to the psychological conditions when constructing textile machinery. We cannot escape the conviction that a permanent economic recovery of our existence within the textile industry of the world is only possible by making the whole industry absolutely as automatic as possible and normalizing it. The rising costs of labour and the social burdens which rise with them, all of which appear as a function of the number of operatives in a factory, imperiously demand for every new mechanism a reduction of the number of persons required to operate it to the utmost. This can only be done when the whole process of manufacture is regarded technically and economically as a single unit, whereby the possibility of uniting certain phases of the manufacture readily follows from the technological conditions of the working process which then makes its appearance. In fact all modern constructions which seek to realize the continuous principle with more or less success have arisen from investigations of this kind. In order to carry out these investigations with necessary clarity, all the factors that exert an influence must be summarized graphically. Thus, for example, the quality which changes from process to process of manufacture, quantity, size, properties, power consumption, water consumption, operatives, raw materials, and so on, must be observed. From this can be seen at once with the aid of the present state of textile technique what technical means are necessary and the most appropriate arrangement of the construction can be settled with ease by means of such a tabulation. From the physiological characteristics of the human being also the most suitable forms can be found for attendance upon the mechanism, whereby the obviousness of the movements must be made as plain as can be done. By this is to be understood, for instance, that a switch motion for switching on and off a motor on a loom is arranged in the same way as the mechanical lever used on a belt-driven loom. In a lifting mechanism the upward movement of the control lever will be used for raising, and the horizontal position for indicating stoppage. If rolls of cloth are moved backwards and forwards, e. g. in measuring machines, the lever must be so arranged that the obvious correspondence of movement is clearly expressed.

An extremely wide field is open to the technique of textile machinery when the experience gained in other technical fields is brought to bear on its problems, and the still young electrotechnique in particular is destined to play a very prominent part. The success that can be achieved here both technically and economically is well shown by the spinning motors of recent construction, one individual electric drive being provided for each spinning spindle, so that all the advantages are made the most use of.

The application of electrotechnical laws to purely textile technical problems is also likely to prove fruitful as the points at which they meet are so universal. It may be recalled that it was only possible to clear up the difficult field of heat conduction and radiation after

thermotechnics succeeded in operating with heating current just as the electric current is used in electrotechnics. When electrotechnical principles are applied in textile technique the prospects for the use of electricity would seem to be very promising.

In this way many auxiliary sciences, special subjects, and empiric sciences are united in the construction of textile machinery and of accessory equipment to make it appear as a branch of technology in general which is scientifically and technically well developed. A branch too which deserves all the more the attention of the technician and the political economist the more it succeeds in strengthening and extending the reputation of German labour, the German spirit of research, and the German instinct for the practical.

Reeding and False Twill

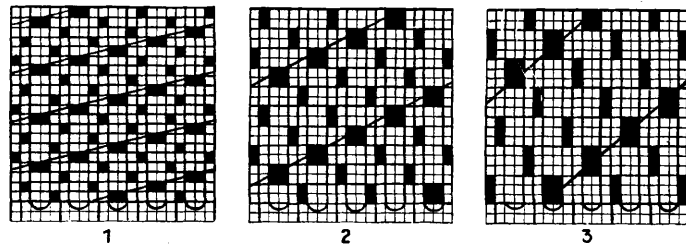
By O. Ehrhardt, jr.

It is well known that the formation of false twill in fabrics of real silk, or artificial silk, or mixtures of artificial silk and cotton, etc., is in some way due to the selection of an unsuitable pitch of the reed. The object of this article is to find a method that is easy of application and permits of predicting from the point paper, *without having to make a practical trial*, before reeding, what pitch is suitable or is liable to form of a false twill with a given weave and sett.

Each wire of the reed occupies a certain space, albeit quite small, among the total of the warp threads, and naturally also forms a lane in the finished fabric, that is, in the intersection of warp and weft according to some system or another. Those branches of manufacture which have to do with fabrics that undergo no further treatment generally try to obliterate these reed marks, but it cannot be done properly with goods that have been dyed in the hank, and similar loom cloths. During weaving the dent presses slightly together the intersection of warp and weft (interlacing point) which I will assume to be ordinarily square (Figure 2), so that it is forced into a rectangular shape. All the interlacing points close to the dent on the right or the left assume a rectangular form instead of the hypothetical square shape, and may produce a twill line in the weave under certain unfavourable conditions, and therefore also

in the finished cloth (Figs. 1—3). For the sake of clarity I have there chosen only one thread line for the threads affected by the reed, and for the unaffected threads in the middle of the space between two dents I took two threads for one.

The line of the false twill can run in any direction, and it would be difficult to predict without a point paper design, but it can also run

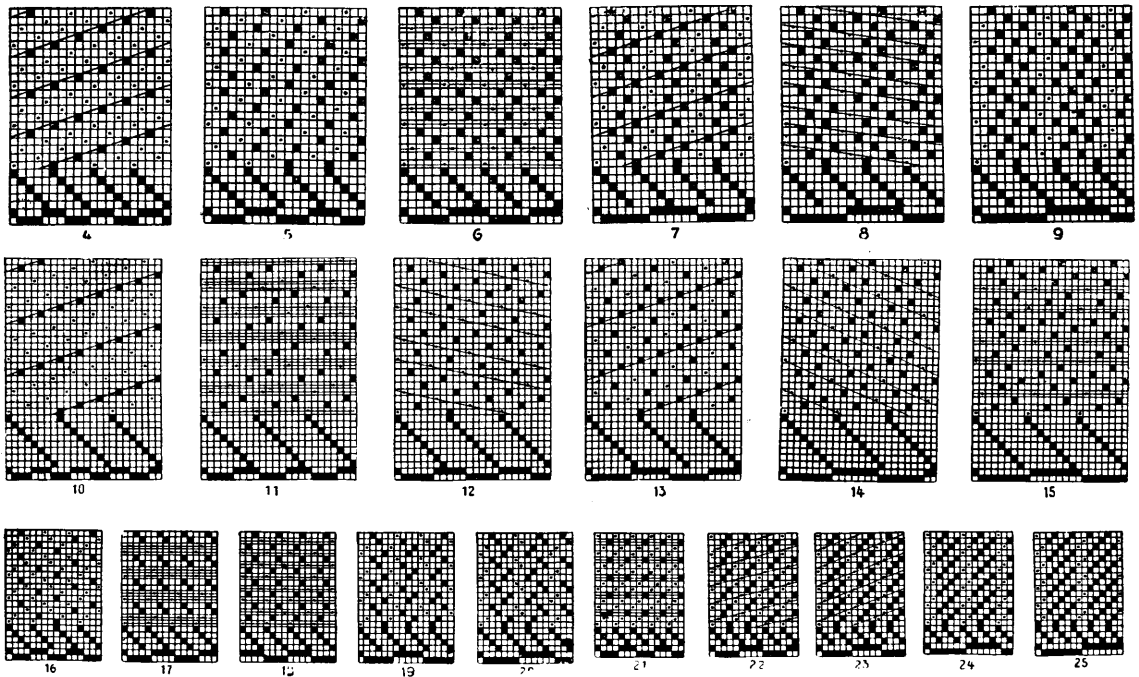


parallel to the direction of the weft and thus cause reediness. This favours the production of weft-streaked goods, in particular when working with only one shuttle (Figs. 6, 11, 15, 17, 18 and 21).

To simplify matters I have represented in the design the various interlacing points which lie some distance apart as being only symbolically different, that is to say, I have only lightly dotted the interlacing points of the threads touched by the dent to the left or to the right, but have shown as full squares those that are isolated from the dents by threads to the right or left. A false twill or a technically perfect cloth is produced accord-

ing as it is possible or not to draw somehow or other a straight line in any direction *through the interlacing points of the one set without being interrupted by the interlacing points of the other set*. To complete the picture, the draft and reeding are added to each weave design from Figure 4 on. The drawing investigation was first carried out on the 5-shaft weft sateen shown in Figures 4—9 (weft sateen was chosen merely for reasons of convenience), then on the 8-shaft weft sateen

appears so prominent because relatively few threads show abnormal interlacing points in the repeat; that is, in the twill line. The fewer the number of threads in the split, the greater is the number of the abnormal intersecting points and the more the twill loses itself, as experience also teaches, the more sharply it runs in the design and finally disappears with three threads (although theoretically still present), and two threads. A consideration of Figures 4—25 leads me to the following results:



shown in Figures 10—15, further on the four-shaft weft cross twill shown in Figures 16—20, and finally on the three-shaft weft twill shown in Figures 21—25, that is to say, in the commonest weaves (apart from plain weave) that are used for real and artificial silk. Of course the remarks here made and the theoretical explanation and the sketches of the origin of false twill apply for all other weaves also. If twill, e. g. eight-shaft fine weft twill 1/7, is examined, it will be found, however, that every sett of the reed, naturally except with one or two threads, causes a reverse twill. Eight-threads produce reed marks, that is, twill in weft direction, as is always the case when the number of the threads drawn into one split is equal to the weave repeat number or to the half of it, Seven threads cause a very prominent reverse twill in the fabric which slopes very flat and

1. 5-thread sateen

Figure 4 3 threads marked twill line

"	5 4	"	good
"	6 5	"	reedy; favours cracks
"	7 6	"	marked twill line
"	8 7	"	less strongly marked twill line
"	9 8	"	good

2. 8-thread sateen

Figure 10 3 threads marked twill line

"	11 4	"	reedy, favours cracks, but in spite of this preferable to all other setts unless 7 threads
"	12 5	"	slight twill line
"	13 6	"	very marked twill line
"	14 7	"	very slight twill line
"	15 8	"	inclined to be reedy

3. 4-thread weft cross twill

Figure 16	3 threads	good
„	17 4	„ very reedy, not to be recommended
„	18 4	„ more regular reediness (dents displaced by one thread)
„	19 5	„ good
„	20 6	„ good

4. 3-thread weft twill

Figure 21	3 threads	not to be recommended; very reedy
„	22 4	„ slight twill line
„	23 5	„ slighter twill line
„	24 6	„ good
„	25 7	„ good

Now it will be found that a false twill produced by unsuitable reeding is enormously increased if a comparatively coarse weft thread is taken instead of one of about the same count as the warp. The reason for this is evident if it is borne in mind that, when a fine weft is used, a thread lying close to the dent and influenced by it forms an interlacing point which, although abnormal, is still in practice almost a square. The deformation only becomes evident when it is made prominent and is pulled out by a coarse weft, say, of stout cotton. Figures 1—3 show this quite clearly, the weft in Figure 3 being thrice as thick as in Figure 1, and in Figure 2 twice as strong as in Figure 1. Otherwise the false twill runs more steeply here too, which means that it is more unpleasant for the eye and all the more prominent.

One other factor appears and that is the connections between the twist angle of the warp and weft threads on the one hand and the direction of the ridge on the other hand (which is partly in evidence in suits with herring bone patterns). It is well known that a ridge gives a closed effect when the spirals of the yarn run in the contrary direction to it. Twist means conservation of energy. The moment that the shed changes when weaving with open shed, the thread raised in the weave repeat becomes slack, which means that the force stored up in the twist has an opportunity to exert itself. This follows somewhat in the direction of the spirals shown in Figure 26, that is to say, towards the left with left-handed twist, and therefore in the case of two-thread reeded fabrics supports in one case the pushing off action of the dent, and in the other case opposes it. In this way

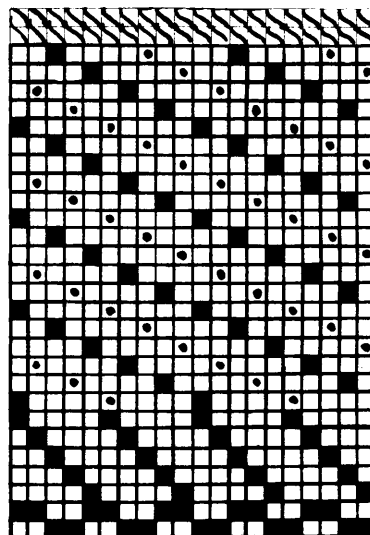
Figure 26 arises. It is thus possible to produce a twill even with two warps per dent.

This twill is further heightened by a left twisted weft (the twist angle runs contrary to the ridge of the false twill) so that even in a mixed silk fabric with two warps per dent

warp: 19/21 den. organzine RL and

weft: 120 den. viscose, weft twist L about 130 twist as described above, a false twill can be produced, which would seem to contradict the theory just set out. If the twisted viscose weft is replaced by an untwisted cuprammonium weft, the effect is diminished very much.

I may sum up as follows. When a false twill is produced, the initial action is set up by the dent pushing the warp aside, which effect is secondarily heightened by the negative action of the twisted warp and weft yarn.



26

The false twill which is formed in the manufacture of cloth, covers, and overcoatings and is the most feared of all must be distinguished from that described above and has quite a different origin. This false twill is caused by unskilful tying of the under weft or the under cloth to the upper weft or the upper fabric. It can be explained on *purely technical weaving grounds* and does not fall within the scope of this article. A false twill in such fabrics, in particular in fabrics with a coarse warp and a rough surface, although theoretically present also in the raw fabric, can be completely obliterated, as mentioned at the outset, by suitable aftertreatment, especially by fulling, washing, raising, or by felting.

The author is well aware that a reference will be found here and there in technical literature to the unpleasant fault of the formation of false twill, but he hopes that he has here indicated a way which permits after due consideration of rapidly finding the most suitable reeding for any given sett. Of course the

density and the nature of the warp set limits which may occasionally prevent the selection of the most suitable reeding practically adapted for a given weave. In such a case the attempt can only be made carefully to weigh already on the design paper the advantages and disadvantages of the reeding in view.

Pneumatic Automatic Feeder

By *W. Mayr*, Chief Instructor

The feeding arrangement for willows and cards consists, as a rule, of a spiked lattice with stripper or of a spiked lattice with transport band and stripper. These arrangements have the great drawback that the material is held fast by the spikes, or is sorted, or becomes entangled, causing a badly mixed layer, indeed it is often necessary to stop work until the feeder has been cleared. Besides this it is tiresome and costs much time to clean

be used for all raw materials employed in the textile industry and that the power consumption is very low.

Figure 1 shows a vertical longitudinal section of the apparatus and Figure 2 a side elevation.

The material is fed into the hopper *g* and passes into the space below *k* through two delivery rollers *h* and *i* connected with one another by toothed wheels, the rollers serv-

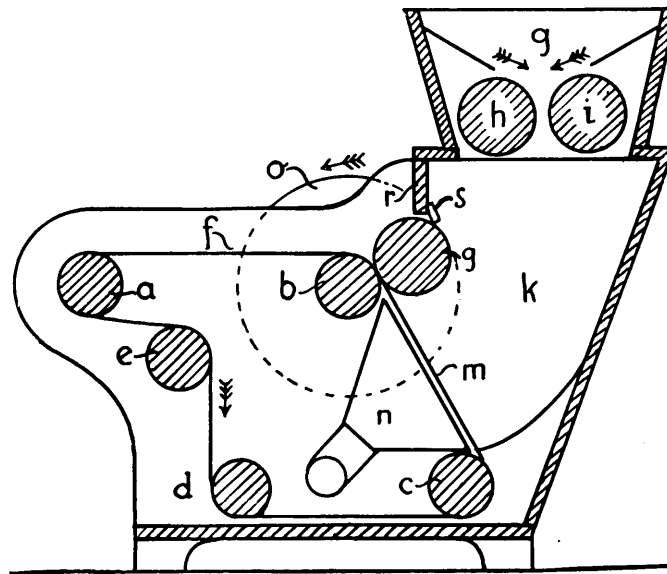


Fig. 1

the feeder after a lot has been run through.

The pneumatic feeder of Heinrich Glass, of Lambrecht, Palatinate (Germany), for which a patent has been applied in Germany (German Patent of Design Nr. 989496) does away with all these drawbacks. Besides this, its construction is extremely simple, so that it is much cheaper than the arrangement hitherto in use, it does not require much space, and it is very easy to clean and to operate. Apart from that the quantity of material fed can be regulated and is always uniform. Finally it may be mentioned that the arrangement can

ing to deliver the material evenly. The endless lattice passes over the rollers *a*, *b*, *c*, *d*, and *e*, and is driven by the belt pulley *o* which is mounted on the axle of the roller *b*. The ends of the rollers *a*, *b*, and *c*, on the other side are provided with toothed wheels which are connected by means of a chain *p* (Figure 2) and serve to drive the lattice regularly. The rate of speed of the lattice can be regulated. A conical suction funnel *n* is mounted between the two rollers *b* and *c* beneath the slanting surface of the lattice *m*, which permits the passage of air, and sucks the material in any

desired quantity by means of a fan situated outside the feeder. The suction surface *m* before the funnel *n* can be made larger or smaller by adjusting the two rollers *b* and *c*. The fluted roller *g* removes the material which has been sucked onto the lattice and delivers it to the vertical surface of the lattice be-

Air is prevented from entering the space *k* by means of a piece of wood *r* with a strip of leather *s* arranged above the fluted roller *g*.

If the willow is furnished with a pneumatic transport equipment, a branch pipe can be built in to connect the pneumatic automatic feeder with the willow.

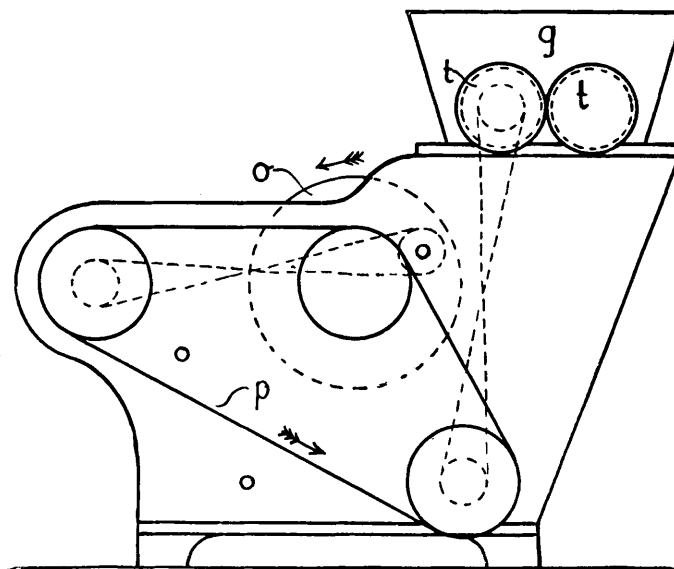


Fig. 2

tween the rollers *a* and *b*, whence it is taken to the next machine. The fluted roller *g* is connected with the guide roller *a* and the feed roller *h* with the guide roller *c* by a crossed rope to regulate their speed properly. The tension of the lattice can be regulated by the roller *e*. The lattice is endless and fastened by patent links which can be loosened; further it can readily be changed and can be replaced in special cases by wirecloth. The fan at the same time removes the dust in the material.

Finally attention should be drawn to a fundamental change in lubricating the wool, if the well known automatic oiling device of J. J. Marx, Lambrecht, is used. The material has hitherto been lubricated on the feed table before the willow, but in the present case it is advisable to mount the spraying nozzle so that the lubricant is finely sprayed onto the material as it falls from the lattice onto the feed table of the willow which lies below it. In this way the loose material is sprayed from all sides.

On the Physics and Chemistry of Dyeing Phenomena

By Professor Dr. K. H. Meyer

IV. On Phenomena observed in the Dyeing of Silk and Wool

By H. Fikentscher and K. H. Meyer

The behaviour of silk towards acids and acid dyestuffs:

The behaviour of silk towards acids and acid dyestuffs has been the subject of constant investigation from many different starting points.

*Gelmo and Suida*¹⁾ studied the influence of acids, alkalies and salts on the dyeing capacity of animal textile fibres. *Walker and Appleyard*²⁾ investigated the adsorption of

1) Gelmo and Suida, *Monatsh. Chem.* 1905, 855; 1906, 225.

2) Walker and Appleyard, *J. of the Chem. Soc.* 69 (1896) 1347.

acids by silk according to the strength of the acids. As they used mainly weak organic acids they failed to observe the law of equivalent absorption of all acids. Georgievicz³⁾ explained the capacity of silk to absorb picric acid and Indigo disulphonic acid by means of the adsorption isotherm. E. Elöd observed occurrences in the weighting and mordanting of animal fibres⁴⁾ and the action on the fibre of the liberated acid, further the influence on the dyeing process of the concentration of hydrogen ions⁵⁾. C. C. Schmidt⁶⁾, Walter M. Scott⁷⁾ and others studied the conditions of equilibrium between acids, acid dyestuffs and silk. Salvaterra⁸⁾ investigated the equivalent absorption of acids by animal fibres by means of numerous acid dyestuffs applied to silk. He did not however obtain a constant equivalent value, apparently because he made his dyeings in a neutral bath, he used too low a concentration and after dyeing rinsed before determining the quantity of dyestuff taken up. When calculated in equivalents his values vary considerably and are generally too low to correspond to the true basic equivalents of silk.

The preparation of the silk:

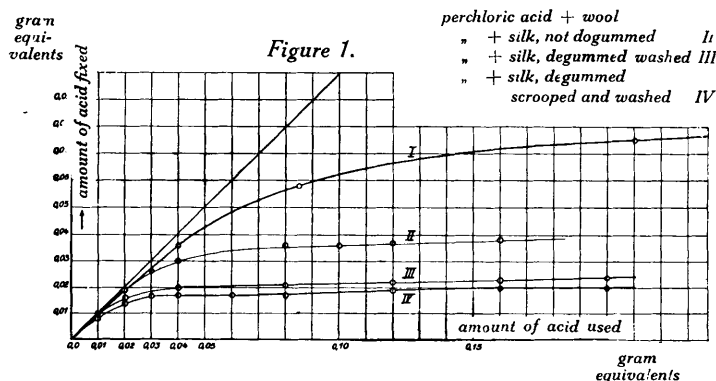
The nature of the silk is of great importance in the following tests. For the experiments described pure natural silk was generally

acid of 0.024 equivalents for 100 gr. silk. If the silk after de-gumming is first "scooped" with dilute acetic acid and then rinsed, the limit value falls to 0.019 probably because certain basic components are dissolved out before de-gumming, i. e. whilst still containing 20% silk gum or sericin, shows 0.038 equivalents; of this figure 0.018 are due to the 75% fibroin and 0.020 equivalents to the 25% sericin so that 100 gr. sericin are capable of combining with 0.08 equivalents perchloric acid, thus equalling the value determined for the wool fibre. The experiments were mainly performed with de-gummed silk because it is in this state that silk is generally dyed and processed.

The water content was repeatedly determined in various samples of silk because silk can absorb a large quantity of water without appearing moist. Under the conditions chosen the water content was found to vary only slightly between 6,3 and 7,3%. It was maintained at a constant figure for the whole lot by storing in large glass flasks with rubber stoppers. The values given refer in all cases to this de-gummed silk, weighed air-dry.

The capacity of silk for taking up acids and acid dyestuffs:

The basic equivalent of silk was determined by its absorption of simple and complex coloured and uncoloured acids from solutions of different concentrations. If a graph is constructed from the figures obtained, the quantities of acid used being plotted on the abscissa



used; it was first de-gummed (freed from sericin) in a warm solution of Marseilles soap free from caustic alkali and then thoroughly rinsed in distilled water. The silk fibroin obtained had a capacity for taking up perchloric

and the quantities taken up by the silk on the ordinate in gramme equivalents, curves are obtained which — as with wool⁹⁾ — at first rise steeply but soon approach a parallel to the abscissa (see figure 1). If a rather high concentration of acid is used the silk is distinctly attacked chemically. New basic groups are set free and at the same time a slight but progressive rise of the limit value takes place.

3) Georgievicz, Monatsh. Chem. 1894, 709; 32 (1911) 1075.
 4) E. Elöd, Kolloidchem. Beih. 19 (1925) 320; Ztschr. angew. Chem. 38 (1925) 199.
 5) E. Elöd, Ztschr. f. ang. Chem. 38 (1925) 837 and 1112.
 6) C. C. Schmidt, Ztschr. phys. Chem. 15 (1894) 60.
 7) W. M. Scott, Ztschr. Chem. 1926 I 2406.
 8) Salvaterra, Monatsh. Chem. 34 (1913) 255; J. prakt. Chem. (2) 88, 502.

9) K. H. Meyer and H. Fikentscher, Melliand Textilberichte VIII (1926) 605.

The conditions were so arranged that equilibrium could be established. 5 gr. de-gummed silk were treated in the thermostat for 5 hours at 54–60° in 200 ccm liquor (and in 400 ccm liquor with the diluted dyestuff solutions) and then allowed to stand overnight at the temperature of the room. Whenever the acids could be titrated with caustic soda the quantity of acid taken up by the silk was determined indirectly by titration of the liquor before and after the test. In the case of dyestuff acids reducible with titanium trichloride the indirect method was frequently checked by the direct titration of the dyestuff on the fibre. The quantities of acid used and fixed were always calculated for 100 gr. silk and then given in equivalents.

The reaction time allowed of 5 hours at 50–60° suffices for the attainment of equilibrium as shown by the tests made with perchloric acid and Orange I acid. (Table I.)

Table 1

Influence of the duration of the reaction on the acid absorption

gramme equivalents of acid (for 100 gr. silk)			
used	fixed		
	5 hours		20 hours
	perchloric acid		
0,020	0,016		0,016
0,040	0,020		0,020
0,080	0,021		0,021
0,120	0,022		0,022
0,161	0,022		0,024
0,216	0,024		0,024
	Orange I acid		
0,095	0,018		0,018

All dyestuff acids can not be obtained in a well crystallised form. The following experiment shows that it is by no means necessary for the determination of the limit value to have the pure dyestuff acid. For the absorption it is immaterial whether the free acid by itself or the dyestuff salt with the addition of an equivalent quantity of a mineral acid is used.

Table 2

Orange I + hydrochloric acid		Orange I free acid	
gramme equivalents		gramme equivalents	
used	fixed	used	fixed
0,022	0,0124	0,022	0,0121
0,045	0,0140	0,044	0,0146
0,064	0,0162	0,066	0,0170
0,086	0,018	0,088	0,0180

In the competition of the two acids for the basic groups of the silk the formation of the salt is brought about first by the acid which yields the more difficultly soluble salt, in this case the dyestuff acid.

A test made of the absorption by silk of the most diverse acids and acid dyestuffs gives a similar picture to that obtained with wool (9), Table 3.

A constant quantity of silk will always fix maximum equivalent quantities of acids, quite independently of the nature of the acid. The values vary more than with wool and lie round a mean of 0.0124.

The values obtained with titanium trichloride are lower than those obtained with caustic soda. Then reason is that the silk gives up to the acid liquor basic constituents which neutralise a portion of the acid in the

liquor and are at the same time titrated by the acidimetric method but not by the reduction method.

Table 3

Name of the acid or dyestuff acid	Molecular or equivalent weight	Concentration	The maximum fixed by 100 gr. silk	
			grammes	gramme equivalents
(titrated with caustic soda)				
perchloric acid..	100,5	$\frac{n}{20}$	2,4	0,024
hydrochloric acid	36,5	$\frac{n}{20}$	0,8	0,022
sulphuric acid ..	$\frac{98,08}{2}$	$\frac{n}{20}$	1,18	0,024
formic acid	46	$\frac{n}{5}$	0,88	0,019
acetic acid.....	60	$\frac{n}{2,5}$	1,44	0,024
benzoic acid	122,5	$\frac{n}{50}$	3,05	(±0,003) 0,025
B-naphthalene sulphonic acid	208,1	$\frac{n}{20}$	6,05	0,029
2.6 naphthol sulphonic acid ..	224,1	$\frac{n}{20}$	6,05	0,027
Naphthol Yellow S	314,1	$\frac{n}{10}$	9,10	0,029
aniline 3.5-di-sulphonic acid > aceto-acetic anilide	$\frac{441}{2}$	$\frac{n}{20}$	6,6	0,030
(titrated with titanium trichloride)				
sulphanilic acid > a-naphthol	328	$\frac{n}{80}$	5,9	0,018
aniline > G Salt	$\frac{408}{2}$	$\frac{n}{20}$	4,28	0,021
O-anisidine > dichlor-benzoyl K acid	$\frac{626}{2}$	$\frac{n}{100}$	6,58	0,021

In the experiments with the free acid of Orange I it was possible owing to the low solubility of its salts to isolate these soluble basic constituents of the silk. If on completion of the test with Orange I the silk is removed from the liquor there appears in the latter gradually, often only after a few days, a precipitate of peculiarly fibrous crystals which show a distinct double refraction and give a Roentgen diagram differing from that obtained with Orange I acid crystals or silk dyed with Orange I. By titrating the Orange I acid contained in the precipitate the molecular weight of the base was determined at about 90. From 100 gr. silk about 0,46–0,66 grammes corresponding to 0,0048–0,0073 gramme equivalents of basic silk constituents go into the liquor which easily explains the difference mentioned.

Accordingly as these soluble silk constituents are considered or neglected the mean limit value is 0.020 or 0.024 gramme equivalents for 100 gr. silk. To fix 1 gramme equi-

valent of acid therefore about 5000 gr. or 4200 gr. of silk are required. The equivalent is thus 3—4 times as great as that of wool, i. e. silk is capable of fixing only $\frac{1}{3}$ — $\frac{1}{4}$ the quantity of acid which can be taken up by wool. This corresponds to the lower affinity in dyeing of the acid dyestuff for silk.

The basic groups of silk are of different strengths corresponding to their varying constitution and are to some extent very weak as is shown by the partial hydrolysis of their salts with mineral acids.

There is of course a still stronger hydrolysis if the weaker organic acids are used (formic, acetic) and this can only be restrained by a large excess of acid. These acids therefore only reach the limit value in a high concentration (see formic and acetic acid, table 3).

Dissolving capacity of silk and wool:

With most monobasic, aromatic acids the limit value is over 0.024 and with some dyestuffs which are mentioned later it is considerably higher. If the possibility of the formation of molecular compounds according to P. Pfeiffers¹⁰⁾ is disregarded this higher figure can only be explained by adsorption or solution. That silk, like acetate silk, is capable of "dissolving" substances will be shown later.

The acid dyestuffs named in Table 4 are all monobasic. They are taken up by the silk much above the equivalent of 0.024 whereas the corresponding dibasic acids appear to behave normally. (Table 3.) Also with wool the results obtained are indicative of solution. (Picric acid Table 4.) But the amount of acid taken up by the wool through the formation of salts is in itself so considerable that it can scarcely be claimed that a further quantity is taken up by solution.

Table 4

Fibre	Dyestuff	Limit value for 100 gr fibre
silk (normal 0,024)	picric acid	0,040
	sulphanilic acid aceto acetic anilide	0,046
	aniline benzoyl S acid	0,037
wool (normal 0.08)	picric acid	0,104

The phenomenon of solution manifests itself even more plainly with the *basic dyestuffs* than with the acid dyestuffs. The acid equivalent of the animal fibres is admittedly not so exactly determinable because of their sensitivity to alkalies, but when $\frac{n}{100}$ caustic soda solution is used there is obtained as the *maxi-*

10) P. Pfeiffer, Ztschr. f. ang. Chem. 39 (1926) 253.

imum value for the acid equivalent of the uninjured fibres a figure of 0.019 gramme equivalents for 100 gr. silk and 0.018 gramme equivalents for 100 gr. wool representing the quantity of alkali taken up. Methylene Blue however is, for example, taken up by the fibres far beyond these values, if care is observed to neutralise with ammonia the hydrochloric acid which is set free. The acid groups present in the silk and wool are not therefore sufficient to neutralise the quantity of dye base taken up. Solution must also have taken place for the salt formation.

Structure of silk:

Silk fibroin shows a crystalline Roentgen diagram¹¹⁾ whereas wool does not. The proportion of the crystalline part to the amorphous is not yet known with accuracy. The question is now whether the crystallites which are not discernible with the microscope enter into the reaction in the same way as the amorphous substance by which they are surrounded or whether for the fixation of the acid it is only the amorphous portion that is mainly active. In favour of the latter assumption is the fact that silk which is saturated with Orange I does not differ in any respect in the Roentgen screen from silk¹²⁾ which is undyed. The crystallites of the dyed silk are thus not measurably affected by the dyestuff which has penetrated to them. It is remarkable that filaments (silkworm)¹³⁾ which are drawn artificially from the gland contents of the silkworm show a much lower capacity for taking up acids and acid dyestuffs than is shown by the natural silk fibres although the origin of both is the same (Table 5).

Table 5

Name of the acid	Limit value	
	for silkworm	for silk (see Table 3)
perchloric acid	0,011	0,024
sulphuric acid	0,010	0,024
p-toluol sulphonic acid ..	0,0105	— —
B ₂ Naphthalene sulphonic acid	0,016	0,029
2:6-Naphthol sulphonic acid	0,014	0,027
sulphanilic acid=α-Naphthol (Orange I acid) ..	0,011	0,018

The limit values for silkworm are about half as high. It is probable that in the natural

11) Herzog, Ber. of the Deutsche Chem. Ges. 53 (1925) 2164.

12) after the researches of Dr. Brill, Oppau.

13) used for angling-line.

spinning process a small portion of the amorphous basic silk gum (see above) with which the silk worm covers his double thread, enters into the fibroin and remains there even when the silk is degummed. From the above results it appears very probable that the crystalline portion does not play a part in the fixation of the acid.

The absorption of o-Nitraniline by silk, wool and other proteins:

The capacity of silk for dissolving dyestuff beyond its equivalent has instigated experiments with inert bodies which do not form salts. They are in fact taken up not only by the silk but also by the wool according to the law of Henry and so present an example of a dissolving process. O-nitraniline which was found to be useful in investigating the dyeing phenomena in the case of cellulose esters¹⁴⁾ has also proved to be the most suitable substance for the present experiment. The dyeings have no fastness whatever but it is just because of this that equilibrium is easily obtained from both sides which is desirable for a solubility test.

The fibres were placed in o-nitraniline solutions of different concentrations and left usually for 14 days at the temperature of the room for complete equilibrium to be obtained. The concentration was determined analytically before and after the experiment by titration with nitrous acid. The colorimetric estimation was rendered difficult because of the liquors becoming more or less cloudy, particularly in the case of the wool. The ratio of concentration in the liquor, i. e. the coefficient of dispersion is shown in the following tables.

Table 6
Dispersion of o-nitraniline between wool and water

grammes nitraniline in 400ccm water used for 5 gr wool	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_W}{C_{Fl}}$
	in 100 ccm liquor C_{Fl}	in 100 gr wool C_W	
0,02	0,0045	0,040	8,9
0,04	0,0089	0,082	9,2
0,08	0,0172	0,220	12,8
0,10	0,0214	0,288	13,4
0,16	0,0345	0,44	12,8
0,24	0,0512	0,70	13,7
0,32	0,0677	0,98	14,4
0,40	0,0840	1,26	15,0

The equilibria in the case of wool nearly obey the law of Henry and do so very closely in the case of silk and silkworm. The coefficient of dispersion for wool comes out at about 14; for silk and silkworm it is the same within the margin of error and shows 24 to 25.

¹⁴⁾ K. H. Meyer and C. Schuster, *Melliand Textilberichte* VI (1925) 737.
K. H. Meyer, C. Schuster and W. Bülow, *Melliand Textilberichte* VII (1926) 29.

Table 7

grammes nitraniline in 400ccm water used for 5 gr silk	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_S}{C_{Fl}}$
	in 100 ccm liquor C_{Fl}	in 100 gr wool C_S	
0,02	0,0038	0,096	25,2
0,04	0,0076	0,192	25,2
0,06	0,0117	0,260	22,6
0,08	0,0152	0,386	25,4
0,12	0,0187	0,508	27,4
0,16	0,0302	0,780	25,8
0,24	0,0455	0,16	25,5
0,32	0,0622	1,42	22,8
0,40	0,0720	1,92	25,2

Table 8
Dispersion of o-nitraniline between silkworm and water

grammes o-Nitraniline in 100ccm water used for 3 gr silkworm	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_{Sw}}{C_{Fl}}$
	in 100 ccm liquor C_{Fl}	in 100 gr silk C_{Sw}	
0,0194	0,0119	0,25	21
0,029	0,0166	0,41	25
0,0388	0,0221	0,56	25
0,0595	0,0346	0,83	24
0,0774	0,0450	1,08	24
0,097	0,0540	1,43	26
			mean 24

If the character of the wool is altered by chemical action the coefficient of dispersion is also altered. For an acetylated wool (about 2—3% acetyl) the following equilibrium was obtained:

Table 9
Dispersion of o-nitraniline between acetylated wool and water

grammes nitraniline in 400 ccm water used for 5 gr acetylated wool	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_{W ac.}}{C_{Fl}}$
	in 100 ccm liquor C_{Fl}	in 100 gr acetylated wool $C_{W ac.}$	
0,02	0,0038	0,096	25,3
0,04	0,0080	0,158	19,8
0,06	0,0118	0,26	22,1
0,08	0,0152	0,386	25,3
0,12	0,0193	0,454	23,5
0,16	0,0325	0,60	18,5
0,24	0,0470	1,04	22,1
0,32	0,0622	1,42	22,8

The fibres formed from protein thus possess very considerable capacity for dissolving. This hitherto unobserved phenomenon is apparently common to all albuminous substances, as the equilibrium determinations with another amorphous albuminous body, a water-insoluble casein, gave the same results:

Table 10
Dispersion of o-nitraniline between casein and water

grammes nitraniline in 100ccm water used for 1,5 gr casein	grammes nitraniline after establishing equilibrium		coefficient of dispersion $\frac{C_K}{C_{FI}}$
	in 100 ccm liquor C_{FI}	in 100 gr casein C_K	
0,01105	0,00828	0,185	22
0,0221	0,0152	0,460	30
0,0414	0,0304	0,733	24
0,0627	0,0447	1,20	27
0,0842	0,0574	1,79	31
0,102	0,0718	2,01	28
			mean 27

The dissolving power of different albuminous substances does not vary essentially; this is evident from a consideration of the very high dissolving power of low acid amides of similar percentage composition. A comparison may be made between the composition of acetyl ethylamine and that of wool and silk:

	wool	silk	fibroin	acetyl ethylamine
	%	%	%	%
Carbon	50	48,5		55
hydrogen	7	6,4		10,3
oxygen	25	26,7		18,4
nitrogen	15—17	18,4		16
sulphur	2—4	—		—

In the case of acetyl butylamine for example it has been found that 100 ccm will dissolve 28.14 gr. o-nitraniline at C°. The solubility of o-nitraniline being 0.1 gr. in 100 ccm water the coefficient of dispersion between acetyl butylamine and water is about:

$$\frac{C_{amide}}{C_{H_2O}} = \frac{28}{0.1} = 280.$$

Between the animal fibres and the cellulose esters there are accordingly only differences in degree in their capacity for dissolving o-nitraniline (see figure 2). With both kinds of fibre the quantity taken up follows the law of Henry and is only very much higher (about ten times) in the case of the cellulose esters than with the animal fibres. (Table 11.)

Table 11

fibre	coefficient of dispersion of o-nitraniline
acetate silk	180
nitro silk	234
silk	25
silkworm	24
wool	14
acetylated wool	25

Conclusion

Silk being an animal fibre and approaching so nearly to wool in its composition, exhibits in the presence of acids and acid dyestuffs a very similar behaviour. It fixes all acids in the form of salts in proportion to their equivalent valents.

The capacity for fixing acid is with wool 3—4 times as great as with silk. The latter however has a very much higher capacity for dissolving monosulphonic acids and inert substances. The process of dyeing animal fibres with acid dyestuffs depends upon both of these operations of solution and salt formation which to some extent overlap one another.

In their dissolving power there is between the cellulose esters and the animal fibres only a difference in degree; the cellulose esters dissolve for example about ten times as much o-nitraniline as is dissolved by the animal fibres.

General observations

In former treatises we have described as solution and not as adsorption the property of taking up substances possessed by acetate silk, nitrocellulose, natural silk and wool in so far as it follows the law of Henry¹⁵⁾. The forces behind these two phenomena are exactly the same and depend upon the molecular attraction between the molecules of the solvent or substrates and the dissolved or adsorbed substance.

The difference is that in a liquid all its molecules exert a molecular attraction whilst with solid "adsorbing" substances only that portion of the molecules or ions lying on the surface can do so for reasons of space. If the quantity of these surface molecules is very large in comparison with the quantity of "adsorbed" molecules we have a similar relationship to that of a dilute solution in a liquid in which the number of the "taking up" mole-

¹⁵⁾ Compare too Georgievicz and Springer, Mon. 21 (1900), 845; Mon. 34 (1913) 744, 751.

cules is very large in comparison with the number of the dissolved molecules.

Correspondingly the quantitative line of the equilibrium curves is with low concentrations also the same in both cases; absorption is a linear function of concentration (Henry's law). In these cases consequently no decision can be arrived at between "solution" and "adsorption" based upon the curves obtained.

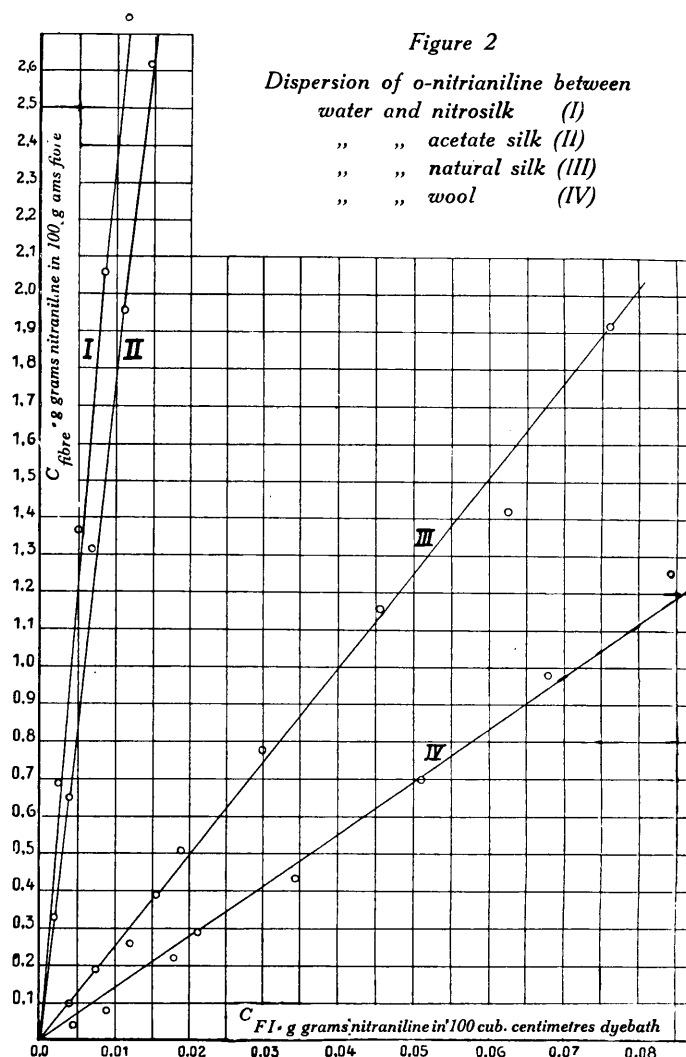
If we will now, as is possible in principle, describe as superficial adsorption the equilibrium curves obtained which up to high concentrations obey Henry's law, we shall be obliged as above explained to assume that the available surface is much larger than the total surface of the adsorbed molecules. This assumption permits of an approximate calculation as we know now that adsorption almost always occurs in a single molecule layer and the area which would be covered by a given quantity of nitraniline in a single molecule layer can be calculated. If the inner surface of the fibre is considered equal to this area and from this is calculated the approximate size of the particles which form the fibre, values are obtained which correspond about to the size of the particle shown by nitro cellulose in a state of solution.

From this it follows that the single particles which form the inner surface of the fibre are identical with the molecules determined in solution, i. e. we can in this case rightly speak of a solution throughout the whole volume.

A similar condition obtains in the case of selective adsorption and the chemical reaction of colloids. The words "selective adsorption" are used to describe the preferential (selective) taking up of certain substances from surface mixtures e. g. in the formation of salts. The formation of salts of the animal fibres appears to us not to be a surface reaction in this sense but a reaction throughout the fibre.

The basic equivalent of wool with a mean of about 1200 is so low that the corresponding reacting particles even if they had to be considered as polyvalent and their equivalent

Figure 2
Dispersion of *o*-nitraniline between
water and nitrosilk (I)
" " acetate silk (II)
" " natural silk (III)
" " wool (IV)



weight of 1200 to be multiplied correspondingly, can be regarded entirely as molecules. Whereas with the cellulose esters and with wool the processes of solution and salt formation bring about equilibria throughout the entire volume without any noticeable effect on the structure or an appearance of surface saturation, with silk the partially crystalline structure appears essentially to influence the dyeing process. As we have seen above the molecules lying within the crystallites of the silk do not take part in the reaction of dyeing. Correspondingly the silk takes up acid dyes far less than wool. In this case where the extraordinary size of the inner surface of the viscous liquid is replaced by the smaller surface of a mixture of crystallites and their intermediary substances, the phenomena of adsorption, surface reaction, are more clearly

apparent. Probably in this way can be explained the tinctorial relationship of natural silk to the chemically dissimilar cotton (with

which adsorption is a decisive factor), this being particularly shown in the behaviour towards substantive dyestuffs.

Studies in Indanthren Colours

By *G. Durst*, Engineer, and *Dr. H. Roth*

We have extended our studies upon Indanthren colours, which were hitherto restricted to Indanthren Blue GCD and RS, to a number of other products some of which exhaust much more slowly, and this characteristic shows itself very plainly in the curves. The first curves which we give below show the exhaustion in the ordinary dyebath, the exhaustion being first controlled every 10 min-

utes and then during the second half of the dyeing every 15 minutes by the determination of the total reduction value. Beneath the curve in each figure which represents the total reduction value, we have plotted the curve of the excess of hydrosulphite in

the form of a dotted curve. The former investigations have shown that this curve runs practically as a straight line, so that the upper curve gives in the main a correct picture of the exhaustion. We have noted under each figure the dyeing recipe so that no further description is necessary (Figures 1 and 2).

In the case of Indanthren Orange RRTS we attempted to follow the exhaustion in vats

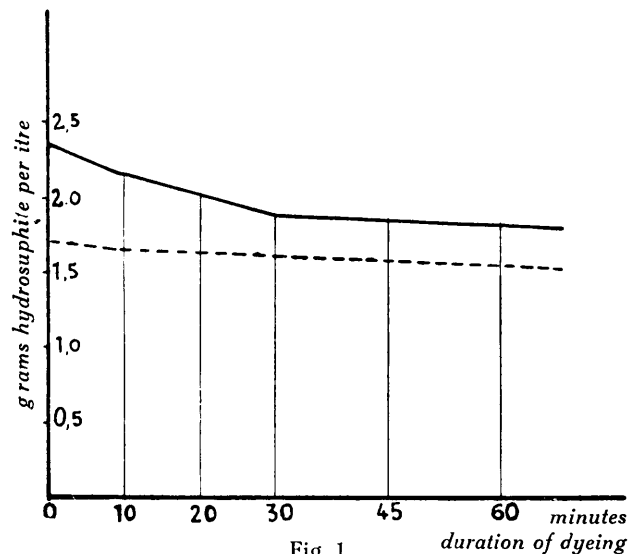


Fig. 1

Curve for Indanthren Yellow GK

1 litre vat contained:

- 0.575 grams Indanthren Yellow GK powder
 - 3.25 „ Hydrosulphite
 - 5 ccm caustic soda 40° Bé
 - 2 „ Turkey red oil 50%
 - 10 grams salt
- dyed for one hour at 30° C

————— total reduction

..... excess of hydrosulphite

utes and then during the second half of the dyeing every 15 minutes by the determination of the total reduction value. Beneath the curve in each figure which represents the total reduction value, we have plotted the curve of the excess of hydrosulphite in

of varying concentration and found, as was to be expected, that exhaustion proceeds much more rapidly in the stronger vats. It is therefore to be recommended to add the dyestuff to the vat in small portions at a time in order to produce level dyeings. (Fig. 3 and 4.)

Apart from this exhaustion of the dyestuffs in dyeing according to the usual recipes, it was also of interest to control the recipes as such. For this purpose we made a dyeing in which we took 6 ccm and 48 ccm caustic soda 40° Bé per litre instead of the 12 ccm prescribed, but in this case did not show the results as curves. It was found that exhaustion proceeds slowest with the use of the normal 12 ccm caustic soda, that it is quite noticeably speeded up with 48 ccm, and that it is increased at a catastrophic rate when too little, say 6 ccm, is taken.

This would seem to indicate disturbances in the state of solution of the vat acid soda which are slight when the quantity of lye is markedly increased, but make the vat useless when too little caustic is added to the vat.

It is much more difficult to follow the behaviour of the vat when the quantity of hydrosulphite added is varied. We used Indanthren Orange RRTS in powder for all our experiments and the vat was set with the following quantities per litre:

- 1 gram Indanthren Orange RRTS powder
- 12 ccm caustic soda 40° Bé
- 4 grams hydrosulphite
- 2 ccm Turkey red oil 50%

In order to test the influence of the hydrosulphite content, vats were set according to this recipe with 2 grams, 4 grams, and 16 grams hydrosulphite per litre. The influence of the oxidation upon the decrease of the excess of hydrosulphite is here so preponderating that the figures of the analysis gave no information. It was also not possible by means of the dyeings produced to evaluate the influence of the varying quantities of hydrosulphite, which proves how desirable it is to be able to determine the dyestuff content analytically. Besides the composition of the vat, the temperature also has a decisive influence upon the exhaustion, and two curves show the behaviour of Indanthren Brown R and Indanthren

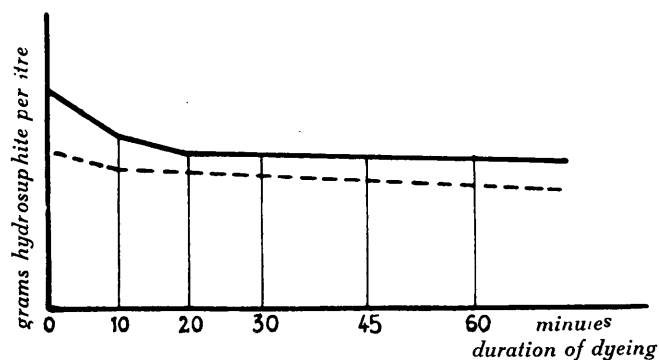


Fig. 2

Curve for Indanthren Brown R

- 1 litre vat contained:
- 0.625 grams Indanthren Brown R powder
- 1.75 " Hydrosulphite
- 5 ccm caustic soda 40° Bé
- 1 " Turkey red oil 50%
- 5 grams salt
- dyed for one hour at from 25—30° C

————— total reduction
 excess of hydrosulphite

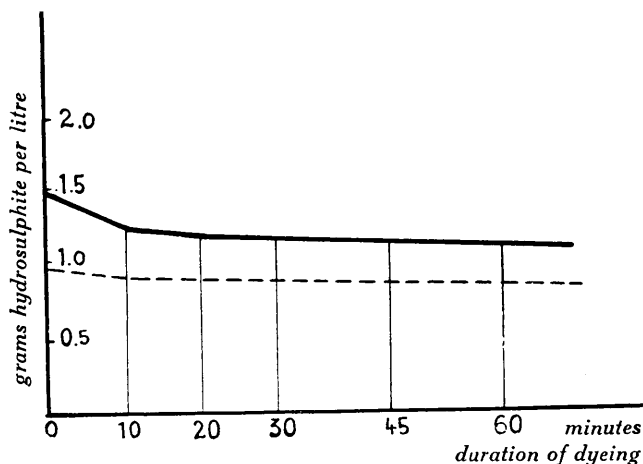


Fig. 3

5% Indanthren Orange RRTS powder

- 1 litre vat contained:
- 0.5 grams Indanthren Orange RRTS powder
- 2 " Hydrosulphite
- 12 ccm caustic soda 40° Bé
- 1 " Turkey red oil 50%
- dyed for one hour at 60° C

————— total reduction
 excess of hydrosulphite

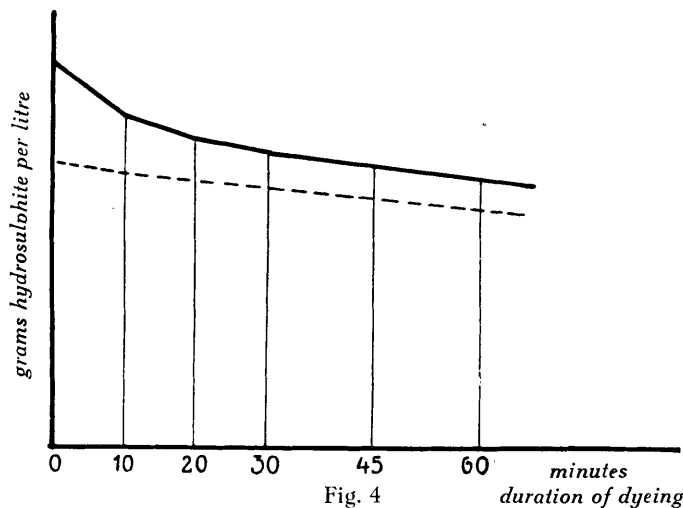
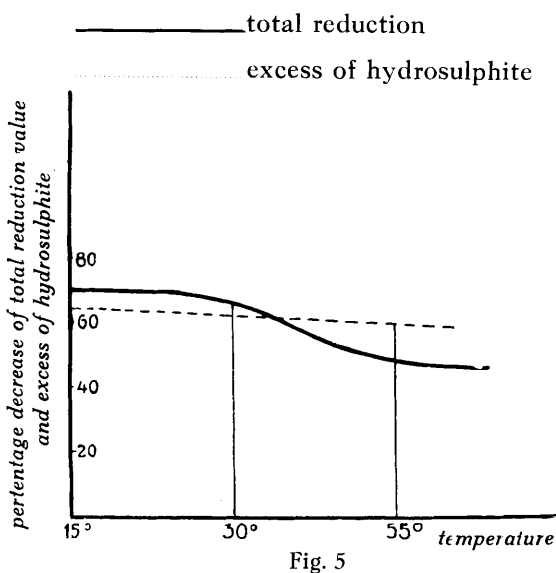


Fig. 4

25% Indanthren Orange RRTS powder
 1 litre vat contained:
 2.5 grams Indanthren Orange RRTS powder
 4 „ Hydrosulphite
 12 ccm caustic soda 40° Bé
 1 „ Turkey red oil 50°/o
 dyed for one hour at from 55—60 C



Temperature curve of Indanthren Brown R
 1 litre vat contained:
 1.25 gram Indanthren Brown R powder
 3.50 „ hydrosulphite
 7 ccm caustic soda 40° Bé
 1 „ Turkey red oil 50°/o
 5 grams salt
 dyed for fifteen minutes

————— total reduction
 excess of hydrosulphite

Orange RRTS at different temperatures. The effect is evidently greater with products that are dyed warm and they exhaust to a much greater extent at a high temperature. The curve for products dyed cold runs flatter, but a stronger exhaustion is found here also when heat is applied (Figures 5 and 6). (The ordinates in Figures 5 and 6 represent the percentage decrease in the total reduction value and in the excess of hydrosulphite.) We have plotted in these diagrams also a curve showing the excess of hydrosulphite which shows clearly that the hydrosulphite oxidation also rises with a rise in temperature.

The dependence of the oxidation of the hydrosulphite is influenced by quite a number of circumstances and we give the following figures in this connection.

(1) Influence of the concentration of the hydrosulphite solution. When the solution was allowed to stand for one hour in an ordinary porcelain dye beaker, one vat lost the following percentage quantities of hydrosulphite at 55° C:

12 grams per litre vat	25 %/o
5 „ „ „ „	15.4 %/o
0.5 „ „ „ „	39 %/o

The vat contained the usual quantities of caustic soda and Turkey red oil besides hydrosulphite. It can be seen that the quantities given in the recipes are the most favourable, while the loss rises proportionately when the hydrosulphite content is raised or lowered. It was to be surmised that stirring the surface would accelerate the oxidation. A test with 5 grams hydrosulphite per litre which lost 15.4% of the Hydrosulphite content at 55° C, lost 29% when stirred, which is practically twice as much.

(2) The influence of the temperature upon the oxidation of the hydrosulphite is shown in the foregoing curves given above but the following figures should still be given:

12 grams hydrosulphite	50° C,	reduction	25 %/o
12 „ „ „ „	20° C,	„	11.7 %/o
5 „ „ „ „	55° C,	„	15.4 %/o
5 „ „ „ „	20° C,	„	11.7 %/o

It is evident from these investigations that dyestuffs which dye in the cold use less hydrosulphite.

sulphite than others which require heat, and that it is most advisable to keep to the quantities given in the recipes, for too much hydrosulphite in the vat will merely lead to a useless loss. This loss of hydrosulphite means

sumes 1 litre caustic soda of 40° Bé. Full consideration must be paid to these conditions, particularly in piece dyeing on the jigger, where a strong oxidation of the hydrosulphite cannot be avoided. We would especially draw

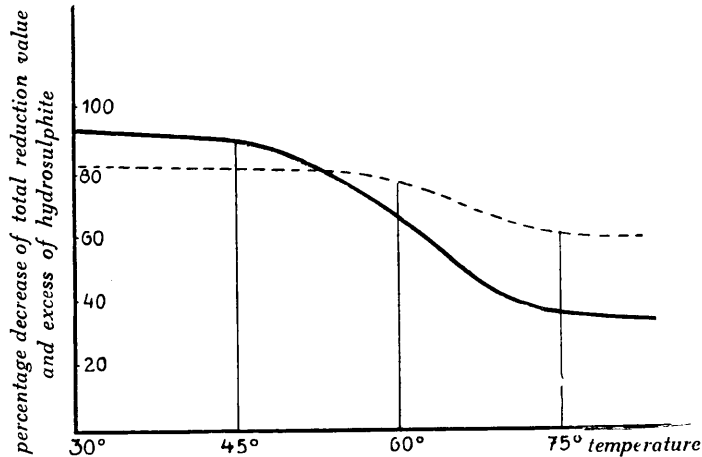


Fig. 6

Temperature curve of Indanthren Orange RRTS

- 1 litre vat contained:
 - 2 grams Indanthren Orange RRTS
 - 3.5 „ Hydrosulphite
 - 12 ccm caustic soda 40° Bé
 - 1 „ Turkey red oil 50 %
dyed for fifteen minutes
- total reduction
excess of hydrosulphite

also a loss of caustic soda, because hydrosulphite forms products with an acid reaction during the oxidation. When completely oxidized, 1 kilo hydrosulphite binds 460 grams caustic soda or 952 ccm of chemically pure caustic soda of 40° Bé. Practically speaking in round figures each kilo of hydrosulphite con-

the attention of anyone who desires to use the analytic processes worked out by us to the fact that they are technically empirical, so that comparable figures can only be secured by strictly adhering to the original conditions, and even then some practice will be required till reliable figures are obtained.

The Application of the Neolan Dyestuffs in Wool and Silk Printing

By Dr. H. Bernhard

On the occasion of the 1925 Colourists Congress in Zürich, Prof. Dr. Ruggli of Basle gave a paper on Neolan dyestuffs which was, however, owing to the position of the series existing at that time and the limited expe-

riences gained by then, confined entirely to the dyeing of Wool. As is well known, this series of dyestuffs is chiefly used for Wool, particularly for the dyeing of fast shades on Loose Wool, Slubbing, Yarn and Piece and

that a special characteristic of the class is the necessity for the use of a somewhat stronger acid bath than usual in dyeing.

Ruggli has already mentioned that the dyeing of Neolan dyestuffs takes place in two phases, the Dyeing and the Development. Since 1925, the Neolan range of dyestuffs has been considerably extended and the Society of Chemical Industry in Basle has, at the same time, investigated the possibilities of their application in other directions. From a close study of their behaviour in the dyeing of Silk, it has been established that entirely different conditions obtain with this fibre than is the case with Wool. In the first place it was discovered that by dyeing with organic acids such as Acetic or Formic, the Neolan Colours gave on Silk shades which are particularly fast to Light, Washing and Water. Development of the ultimate shade and fastness as a secondary phase has not been observed. Another notable characteristic found, is that in contrast to other classes of dyestuffs, the Neolan Colours dye both Pure and Weighted Silk the same or practically the same depth of shade. Furthermore they exhibit good level dyeing properties on weighted Silk.

The successful results obtained in Silk dyeing led to experiments in the printing of Silk with Neolan Colours. From this branch of the trade there is a constant demand for faster colours. Hitherto, the fastest effects in Silk printing were only obtainable with Vat Colours which mostly lacked brilliance and further the application from a Potash printing colour was not always regarded with favour. Printing with Chrome Printing Colours, while generally producing effects of good fastness, leaves a harsh "feel" or handle on the material. A study of the behaviour of the Neolan Colours in the printing of Silk showed that in this case, the Chrome in its particular form of combination, did not exercise any unfavourable effect while the printed effects so produced were perfectly fixed and could be described as of excellent fastness to Light and Washing. Hitherto, in the production of heavy "Blotches" no tendency to "bleed" had been observed. It is noteworthy that the Neolan Colours can be printed without or with only a small addition of Acetate of Chrome and except for somewhat of an increase in the fastness to Water in the latter case do not exhibit any appreciable differences.

The following printing instructions give an idea of the method of applying the Neolan

Colours in Silk Printing. The same recipes can be used for the printing of Chiné. It should be mentioned that the addition of Organic Acids to the printing colour is not necessary and are preferably omitted, as certain Neolan Colours, i. e. Neolan Green B and BL conc. and Neolan Dark Green B do not develop in presence of Acid. If Acetate of Chrome is used an addition of Ammonium Tartrate 32° Tw. is also recommended.

Printing Recipe I without Chrome.

10— 30 gr. Dyestuff are dissolved in
400 cc. boiling water, stirred into
600 gr. hot British Gum Thickening 1 : 1,
boiled up and stirred until cool.

Printing Recipe II with Acetate of Chrome.

10— 30 gr. Dyestuff are dissolved in
350 cc. boiling water, stirred into
600 gr. hot British Gum Thickening 1 : 1,
and stirred until cold, then add
25— 40 cc. Acetate of Chrome 32° Tw. and
5— 10 cc. Ammonium Tartrate 32° Tw.

While in general from 5—30 gr. Dyestuff per kilo is sufficient for colours, in the case of Neolan Blacks printed with 60 gr. dyestuff per kilo, an addition of 30—60 cc. Acetate of Chrome 32° Tw. and 10 cc. Ammonium Tartrate 32° Tw. is recommended.

After printing, steam for 1 hour without pressure, wash and finish as usual. Shorter steaming as a rule is not conducive to complete fixation of the Neolan Colours.

Latterly an increasing amount of Spray Printing is being done on silk for which the same recipes may be used, omitting only part of the Thickening.

The following Neolan dyestuffs are suitable for the printing of Silk:

Neolan Yellow G, GR and R,
" Orange G and R,
" Pink B and G,
" Red R,
" Bordeaux R,
" Blue B, BR, G, 2G, GR and 2R,
" Green B and BL conc.,
" Dark Green B,
" Brown GR and GRA,
" Violet Brown B,
" Violet R,
" Black B and 2R.

THE PRINTING OF WOOL with the various classes of dyestuffs is governed by similar conditions as the printing of Silk. In

Woollen piece printing, Chrome colours are not often used as also in this case the addition of Chrome Salts has a tendency to produce a harsh "feel" on the goods. The work is therefore confined largely to Basic, Direct and Acid Colours, with consequently the production of effects of inferior fastness. As in Silk printing, the use of colours not capable of being completely fixed also produces the possibilities of "marking off" or "bleeding" of heavy Blotches. Vat Colours have been tried, they are printed from a Potash printing colour and yield very fast results. At the same time they exhibit the fault, that the end effect i. e. the complete development, is difficult to attain.

For these reasons there has also existed in the Woollen printing trade, a demand for a class of dyestuffs which could be applied either with or without a small addition of Mordant to yield printed effects fast to Light, Washing, Water, Perspiration etc., and at the same time show no tendency to "mark off" or "bleed" in heavy Blotches. The trials showed that this was possible with Neolan Colours and led to the following recipes being suggested. The steaming in this case, evidently produces complete development which in dyeing is only attained by an energetic boiling in presence of an increased amount of Acid. The addition of Chrome is not absolutely necessary but at the same time a small addition improves somewhat the fastness to Water. The addition of Acid is also omitted.

Printing Recipe I without Chrome.

10— 30 gr. Dyestuff are dissolved in
400 cc. boiling water, stirred into
600 gr. hot British Gum Thickening
1 : 1, and boiled up. Add
70 gr. Glycerine and stir of Chrome.

Printing Recipe II with addition of Chrome.

10— 30 gr. Dyestuff are dissolved in
290 cc. boiling water, stirred into
600 gr. hot British Gum Thickening
1 : 1, and boiled up. Stir until cold
and add
50 gr. Glycerine and
60 cc. Acetate of Chrome 32° Tw.

Print on, dry and steam moist for 1 hour. Wash and finish as usual.

The Neolan dyestuffs suitable for Wool printing are the same as given in foregoing list for Silk printing.

Recently there has been a revival of interest in Vigoureux printing and the application of the Neolan Dyestuffs in this branch of the trade has therefore been studied. The fastness requirements in Vigoureux printing differ from those in Woollen piece printing as Slubbing is a prior stage of manufacture and the processes of Spinning, Weaving and often Milling have to be taken into consideration. Generally the Slubbing is spun into either Hosiery or Weaving Yarns. In the first case the goods are not subjected to a Fulling process while in the second case severe Milling is given, which demands a corresponding fastness in the dyed shades. For Vigoureux printing for the production of the ordinary Knitted fabric and Ladies Dress Goods a good selection of dyestuffs is available which exhibit good fastness to Light. Latterly, however, there has arisen a demand for fast to Light, Washing, Water and Perspiration effects for Tricot, Dress Goods etc. Trials made with Neolan printed Slubbing showed that unexpectedly fast results were obtained which were suitable for fast tricot fabrics and even for the best quality Dress materials. For this latter article, Chrome colours were hitherto chiefly used. The Neolan Colours, however, exhibit equally fast and brighter shades without any difficulties of fixation. When using Chrome colours, fixation is only attained by the addition of Acetate of Chrome, Fluoride of Chrome, Chromaline etc., according to the dyestuff in question. For the fastest effects a large addition of Chrome Salt is usually required which often leaves a "harsh" feel on the Slubbing. The Neolan Colours can be printed either with or without Chrome and even in the former case, the Chrome Salt addition is only small, thus lessening the danger of any adverse effect on the material.

The Recipes for Vigoureux printing with Neolan Colours are very similar to those suggested for Woollen piece. As Slubbing can carry somewhat more Chrome, the amount may be increased as given in the following recipe. At the same time it should be understood that the necessary fastness is also attained without the addition of Chrome and the Backwashing bath remains clear.

Printing Recipe with slightly increased addition of Chrome Salt.

10— 60 gr. Dyestuff are dissolved in
300 cc. boiling water, stirred into

500 gr. hot British Gum Thickening
1:1, boiled up and stirred until
cold. Then add
40 gr. Glycerine and
20—100 cc. Acetate of Chrome 32° Tw.

After printing, wrap in cloth and steam in a moist condition. One hour's steaming at $\frac{1}{4}$ atm. pressure will be found sufficient. If a pressure steamer is not available, the steaming can be carried out in an open Steam Chest. Should it be necessary, for technical reasons to dry after printing, the use of moist steam is advisable. After steaming, the Slubbing is passed through the Back-washer in which the first bath should contain luke-warm water while the second and third are used for soaping and washing respectively, finally drying and melanging in the Gill-box.

DISCHARGE PRINTING

A. Silk

Following the demonstration of the fact that shades of excellent fastness to Light, Washing and Water could be produced on Silk with Neolan colours, the question of the dischargeability of such dyeings naturally arose. It is well known that Mordant dyestuffs which have been fixed with Chrome are only dischargeable in very pale shades as the Chrome on the fibre leaves a greyish impurity in the whites. The addition of Ammonium Tartrate, Citrate or Oxalate to the discharge printing colour effects only a slight improvement. It is therefore rather interesting to record that dyeings of the peculiar Chrome combination represented by the Neolan class of dyestuffs can be easily and completely discharged with Hydrosulphite preparations. As the printer well knows, one general recipe for discharge printing on Silk cannot be used in every case without some modification as the Tin-Phosphate weighting, where weighted Silk pieces come into question, exercises an influence on the dischargeability. It has been shown that weighted pieces can only be discharged with a printing colour containing Zinc Oxide.

The preparation of a printing colour which gives good results on weighted Silk piece is as follows:

450 gr. Gum Thickenings 1:1,
400 gr. Hydrosulphite RWS Ciba,
150 cc. Water.

1 Kilo.

(The addition of Zinc Oxide can be reduced or omitted entirely in the discharging of Pure or slightly weighted Silk.)

After steaming in the Mather & Platt, wash and finish as usual. Coloured discharges can be produced in the usual manner with Basic, Acid or Chrome colours.

The following Neolan dyestuffs are suitable for dyeing ground shades for discharge work:

Neolan Yellow G and R,
,, Orange G and R,
,, Brown GRA,
,, Violet Brown B,
,, Pink B and G,
,, Red R,
,, Bordeaux R,
,, Violet R,
,, Blue B, BR, G, 2G, GR and 2R,
,, Green B and BL con.,
,, Dark Green B,
,, Black B and 2R.

B. Wool

For discharge printing on Woollen piece, selected Acid colours have hitherto chiefly been used, special consideration being paid to their level dyeing properties, as the material is mostly chlorinated. It has now been established that the Neolan colours on Wool are in most cases dischargeable with Hydrosulphite preparations. The Chrome occurring in the Neolan complex does not interfere with the production of a satisfactory white discharge which, apparently, would indicate that the Chrome on the fibre exists in some different form of combination than is the case with ordinary Mordant colours. With Neolan dyestuffs it is now possible to dye shades fast to Light, Washing, Water and Perspiration on which can be produced discharge styles of the highest degree of fastness, hitherto not possible with ordinary Acid colours.

The recipes for the preparation of discharge printing colours are similar to those in general use for wool. The White discharge colour contains an addition of Zinc Oxide or Hydrosulphite preparation containing Zinc Oxide.

The following general recipe yields good results on full dyed grounds:

230 gr. Gum Thickenings 1:1,
500 gr. Hydrosulphite RWS Ciba,
130 gr. Glycerine,
100 cc. Albumen Solution 1:1.

1 Kilo.



According to the depth of shade, the amounts of Hyrosulphite preparation and Albumen can be reduced.

Coloured discharges are made up as usual for discharge printing on Wool with Basic or Acid dyestuffs.

The following Neolan dyestuffs are recommended for the dyeing of ground shades for discharge work:

- Neolan Yellow G and R,
- „ Orange R,
- „ Brown GRA,
- „ Violet Brown B,
- „ Red R (only in pale shades),
- „ Bordeaux R,

- Neolan Violet R,
- „ Blue 2R,
- „ Green B and BL conc.,
- „ Dark Green B,
- „ Black B.

The foregoing only purports to be a short description of the application of the Neolan Colours in direct Printing and Discharge styles on Silk and Wool in which perforce all possibilities could not be outlined. Further Work done in the practical application of the Neolan Colours in the print works will perhaps allow to form a definite opinion on the application of the Neolan Colours in Printing of Wool and Silk.

Steam Aniline Black

By Professor *N. Wosnessensky*

I. Introduction

Aniline black is one of the most beautiful and stablest of colours and can truly be called the best and fastest black of all. It is very

widely used for dyeing and for calico printing owing to the simple and cheap dyeing process, and on account of its important properties, such as beauty of shade and fastness.

Unfortunately the process is to a certain extent poisonous so that this method of working ought, as a matter of fact, to be forbidden. The use of aniline in dyeing and calico printing ought, as a matter of fact, to be forbidden, just as work with arsenic compounds is forbidden. But this cheap and most stable colour is irreplaceable at the present stage of dye-stuff chemistry, and textile chemists and hygienists must accordingly try in every way to lessen the danger which is inherent in the use of aniline oil in the textile industry.

This problem can be solved in two directions. Firstly, either the equipment of the workroom must be changed, or, secondly, the quantity of aniline required in the dyeing methods must be reduced. The latter possibility will be here considered.

II. Literature

Before we make any attempt to change any processes, it will be advisable to consider what has been written upon the subject. In this connection the following authors should be mentioned:

1. Noelting, *Anilinschwarz*, 2nd ed, 1904.
2. Knecht-Fothergill, *Textile Printing*, 2nd edition.
3. Ullmann, *Encyclopädie der technischen Chemie*.
4. Heermann, *Technologie der Textilveredlung*.
5. Axmacher, *Führer durch den Zeugdruck*.
6. Lauber, *Handbuch des Zeugdrucks*.
7. Braß, *Praktikum der Färberei und Druckerei*.
8. Gnehm-Muralt, *Taschenbuch der Färberei und Druckerei*.
9. Depierre, *Traité de l'impression*.
10. *Farbwerke Höchst*, Ratgeber.

The following tabular survey gives a summary of the processes given in these sources.

This table was prepared as follows. In order to secure comparable figures, we have calculated them afresh and reduced them to 1 kilo printing colour (columns 5, 6, 7, 8, 9). Then the total quantity of aniline used was worked out (columns 10, 11), and the corresponding quantities of oxidizing agents (column 3) and K_4FeCN_6 calculated and expressed in percentages of aniline¹).

The average figure for aniline — 78 grams — is much too high, but such an excess of

1) These figures have been calculated by several authors on aniline chlorhydrate, but this is wrong, because several salts of aniline are used. We have accordingly regarded the total content of aniline as the main point, which is of great importance for us.

aniline can be explained by the further discussion of the question. According to these statements about one half of the aniline used is lost in the air, and this fact is confirmed by our being able to produce a good black with 40 grams of aniline per kilo printing paste.

The tabular statement shows that there is not much agreement among the various authorities, so that there remains to be decided which method is correct.

Our investigations will cover three points, corresponding to the three constituents of aniline black.

A. We must first of all determine how far the aniline salts can sublime and decide the question whether the presence of free aniline in the colour is necessary.

B. We must further determine just what part potassium ferrocyanide plays and fix the quantity required accordingly.

C. Finally the quantity of oxidizing agent must be determined that is required to oxidize the aniline used, so as to prevent any loss of it if sufficient oxidizing agent is not present.

A. M. Tschilikin was the first to point out in the literature that free aniline is to be found in the dye liquor which partly evaporates off during drying. The same applies to the printing colour and it can be said in advance that the whole of the aniline in the colour should be neutralized.

According to M. Tschilikin (cf. "Nachrichten")²) the quantity of aniline recovered amounts to from 8—12 per cent., but we must recover 50% of the aniline used.

We have therefore to rely upon the complete neutralization of aniline. The question is now, as it was then, whether the excess of aniline can be avoided.

There are several processes according to which the whole of the aniline is to be neutralized (No. 6, 7, 8, 18), but the authors use an excess of aniline.

III. Calculating the quantity of potassium ferrocyanide

B) The nature of this calculation depends upon the part ascribed to the salt. Many authors look upon it as a catalyst, but this would appear not to be correct. Others again (Noelting, page 66; Georgiewics, page 268) state that KCl and the corresponding salt of aniline are formed in the solution. It should be observed that this aniline salt was pre-

2) *Izvesti ya textilnoy Promischlennosti*, 1925, Nr. 32, page 24. *Melliand Textilberichte*, 1927, Nr. 3.

Table 1

		page	percentage calculated on aniline		per kilo printing colour			per kilo printing colour		aniline		
			Na ClO ₃	K ₄ Fe CN ₆	aniline salt	free aniline	total aniline	Na ClO ₃	K ₄ Fe CN ₆	neutral. with HCl	free	
1	Noelting	30	48	80			82	39	66	64	18	(NH ₄) ₄ FeCN ₆ aniline ferrocyanide
2	—	52	58	49			83	49	41	75	8	
3	—	52	53	59			85	45	50	76	9	(on tannin ground)
4	—	75	50	55			70	35	38	53	17	
5	—	64	40	43			82	33	36	63	19	on wool (26 tartaric acid)
6	—	112	52	90	133		96	50	87	96	0	
7	—	113	55	69	132		95	50	66	95	0	on wool
8	Knecht	305	46	101	84		60	28	61	60	0	
9	Ullmann IV	159	41	68	95	5	73	30	50	68	5	55 p. thousand lactic acid
10	Heermann	343	40	35	45	55	87	35	30	32	55	
11	—	492	41	68	99	9	80	33	55	71	9	42 K ₃ Fe CN ₆ 33 KClO ₃ 7 tartaric acid 44 acetic acid
12	Axmacher	187	53	59			85	45	50			
13	Lauber	399	57	(74)			56	29	42	38	18	
14	—	399	47	86	82	14	72	34	62	59	14	55 p. thousand formic acid
15	Brass	72	34	68	95	5	73	25	50	68	5	
16	Gnehm	73	63	71	85	5	63	40	45	58	5	55 p. thousand formic acid
17	Depierre I	425	40	6	104	35	113	45	7	78	35	
18	— III	129	73	108	71		51	38	55	51	0	
19	Farbwerke	288	34	68	94	5	72	25	50	67	5	
20	German Patent 275,845		40	35	45	55	87	35	30	32	55	
			48	65			78					

pared by itself according to earlier processes (Noelting, page 52).

In the latter case an equivalent quantity of K₄FeCN₆ must be taken, that is to say, an amount must be taken equal to 113.6% of the quantity of aniline used. The goods are thereby protected from being attacked by the hydrochloric acid set free, because it is neutralized quantitatively to KCl.

IV. Calculation of the necessary quantity of oxidizing agent

C) It is advisable, in order to make use of the whole quantity of aniline taken, to oxidize it as quickly as possible, so that it cannot sublimate off the fabric again.

We are even of the opinion that if working is done properly with following oxidation (e. g. by treating the goods with bichromate) it cannot be calculated at all. The unoxidized aniline adhering to the goods would have partially evaporated in the course of the vari-

ous treatments to which the fabric is subjected and would therefore be lost. Accordingly it is advisable to conclude that the formula of the quadruple quinoid hydrolyzed aniline of Willstätter (Berichte 42—44) is correct.

During the transformation from aniline to the substance mentioned 8 molecules of aniline lose 25 atoms of hydrogen, that is to say, we must use $\frac{12.5}{3}$ molecules of potassium chlorate, that is, 59.5% of the weight of the aniline.

Willstätter himself points out (Berichte 42—4128) that 61% chlorate salt are required for the preparation of the quadruple quinoid aniline (he himself used the potassium salt and worked with vanadium). He probably convinced himself that part of the oxygen is lost, and the theoretical figure given above can be regarded as a minimum.

In oxidizing K₄FeCN₆ to K₃FeCN₆ a certain

amount of oxidizing agent is consumed, amounting to about 5% of the weight of aniline.

In this way the total quantity of oxidizing agent is 64% sodium chlorate calculated on the weight of the aniline.

V. Normal process

When the tabulation given above is examined, it will be found that none of the processes given satisfy the conditions just mentioned, but it should be mentioned that process No. 18, according to which the quantity of chlorate even exceeds the theoretical amount, gives the minimum quantity of aniline (reckoned on 1 kilo colour). The other processes deviate even more from the theoretical figures and consequently give larger quantities of aniline. Process No. 17 is of special interest, because it calls for the smallest amount of K_4FeCN_6 and thus yields the largest quantity of aniline.

Upon looking through the various processes which have been reported in the literature of the past fifty years and more it can be seen that their authors have not followed any general leading idea.

VI. Experimental investigation

It is known from the literature that the aniline salts (in particular the aniline salts of organic acids) sublimate and their volatility has several times been determined.

Nowhere, however, is there any reference to the volatility of aniline ferrocyanide. If we accept the formation of this salt, its volatility is of great importance for us.

This investigation is conducted by diazotizing the aniline in combination with sulphuric acid, which is best done by using 4 molecules H_2SO_4 to 1 molecule aniline. The results are shown in the following table which gives the percentage figures directly.

	Aniline content before drying	after drying at 60°C		Loss
		on the fabrik	in the solvent	
Chlorhydrate .	100%	82,3	15,7	2
Tartrate	100%	93,9	4,31	1,79
Ferrocyanide . .	100%	80	9,21	10,79

The small loss shown in the first two analyses indicates that they were comparatively exact. The excessive loss in the third case is striking, but it can easily be explained. The third test on white fabric impregnated

with the aniline salt dyed greyish brown in contrast to the other two. It is thus proved that part of the aniline was oxidized and was lost for the analysis.

The latter observation permits us to explain the part played by potassium ferrocyanide: the aniline ferrocyanide can be oxidized even in the air.

VII. Working process

The calculations quoted above give us the practical application. There were taken 40 grams aniline (figured on 1 kilo colour), 45 grams K_4FeCN_6 (100% of the theoretical), 26 grams, later 28 grams, chlorate (that is, 60—70%; rather more than theoretically required).

It was thereby found that the shade of aniline black becomes reddish in the strong oxidation and that the aniline is not completely used up when the oxidation is insufficient, as can better be seen when letting down the colour.

The use of tartaric acid makes the shade greener. (The salts formed are potassium tartrate and the corresponding salt of aniline. The fine crystals of the precipitate which mix with the printing colour do not cause the slightest trouble.) The result was good and the goods were first printed according to the following recipe:

- 40 aniline
- 40 HCl 19° Bé
- 822 thickening and water
- 50 K_4FeCN_6
- 20 tartaric acid
- 26 sodium chlorate

made up to 1000.

Then the amount of potassium ferrocyanide was reduced to 40 grams without having much effect upon the strength of the fabric.

In one mill thousands of pieces were printed in this way and in many others test runs were made.

It is further evident that good results are obtained without tartaric acid if the whole of the aniline oil is carefully neutralized. If tartaric acid is not used, the more delicate parts of the pattern appear rather reddish, which is particularly noticeable when the prints are made with only 30 grams aniline per kilo (that is to say when let down 3/1). On the whole, however, the results are quite satisfactory. The strength of the goods is better than formerly when free aniline was

used, losing, as they do, only from 8—10% in strength. After the prints have been steamed for a short time, they can be steamed for one hour longer without adding chloride of ammonia, after which the strength of the goods is 97%, taking the strength after the short steaming as 100 per cent.

These tests give us the following recipe:

- 40 aniline oil
- HCl till completely neutralized
- thickening
- 40 potassium ferrocyanide
- 26 sodium chlorate

made up to 1000.

Many thousands of pieces were printed with aniline black according to this recipe

in the works of the Trechgornaia Manufaktur³⁾.

The printing colour suffers no change within one to two days. After that it turns darker, but that causes no trouble.

In regard to health conditions, it is to be recommended to use aniline salt which has been prepared beforehand instead of aniline oil with acid, because aniline salt is less dangerous. The quantity of chlorate depends upon its dryness and upon the conditions in the Mather-Platt ager, and can vary from 60 to 70% of the weight of aniline taken.

In the next article we shall discuss the aniline black padding solutions which are of special interest.

³⁾ Formerly Prochoroff Works.

The Spectrodensograph, a Registering Apparatus for Determining the Absorption Curves of Dyestuffs

By Professor *E. Goldberg*

A Technical Communication from the International Society of Chemists and Colourists

The chemical qualities of coloured substances have been carefully investigated, but our knowledge of their optical constants lags far behind, although it is just these which settle the practical use of the colouring matters. The reason for this remarkable state of affairs is that there has not existed until now a simple means of determining in figures the composition of the light reflected by a coloured body or transmitted through it. Of course the spectrum informs us most perfectly upon this head, but it must be admitted that the absorption spectrum does not by itself define the appearance of a colour, that is to say, its shade, although it settles this. On this account a number of attempts have been made to express the appearance of a colour in numbers by means of some colour system, but in spite of this the absorption spectrum is still the most important characteristic of every coloured substance from the optical point of view.

Absorption spectra are at present generally found by the aid of a spectrophotometer or spectrographically, but the use of these apparatus is very tiresome. When working with the spectrophotometer the extinction coefficient must be determined, that is to say, the weakening of the light in each spectral division, and the curve plotted. The photometrical part of the work is tedious and not exactly pleasant. Light which has passed

through a colouring matter and has been split up spectrally is not very strong, particularly at the blue end of the spectrum, even when powerful sources of light are used. The work must consequently be done in a darkened room and is inclined to strain the eyes, because a lamp must be switched on each time a photometric reading is made which always destroys the heightened sensitiveness of the eye produced in a short time by the darkness. The calculation and plotting of the curve is a fertile source of error. When measuring in deep red, blue, and violet, the yellow and yellowish green part of the spectrum causes most disturbance by reflexions within the photometer unless care has been taken beforehand by the use of a monochromator that only that part of the spectrum which is actually being measured at the moment shall reach the photometer itself. But the use of the monochromator brings with it the further great disadvantage that not merely the photometer, but also the monochromator must be adjusted at every new measurement to the new spectral field.

This is probably the reason why an atlas of the absorption curves of the organic dyes does not exist even at the present day.

The spectrodensograph is intended to afford the possibility of determining in the simplest way the absorption curves of colouring matters, that is to say, of coloured solu-

tions and of colourations. This instrument is really the application of the densograph to the technics of spectral analysis and was completely constructed already in 1914 by the author in collaboration with Mr. André Callier, of Ghent. Owing to the war publication has been delayed until now.

The apparatus is shown in Figure 1 and consists, as can be seen from Figure 2, of two separate parts which are so connected that they can be simultaneously adjusted. The first part (I) is a monochromator comprising the source of light l (Wolfram point arc lamp), the collimator lens k_1 , the prism p_1 , and the objective o_1 . The latter is a double

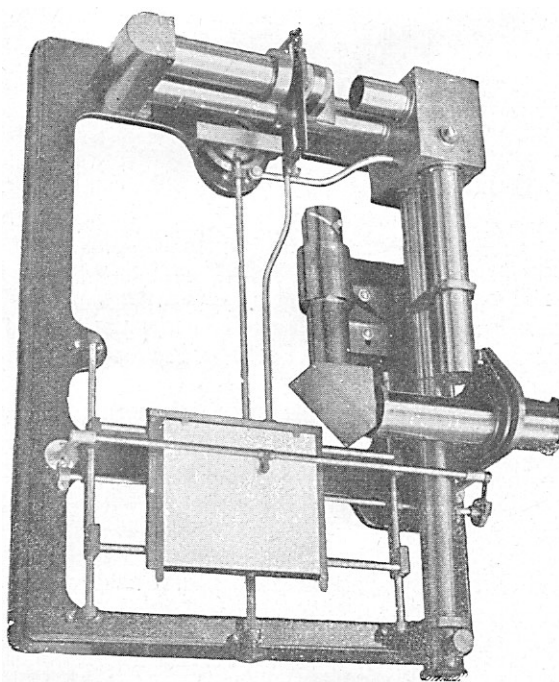


Fig. 1

lens such as is generally used to illuminate spectrometers (Figure 3), so that two small spectra of the source of light, which serves in this case as a slit, are formed in the focal plane of the objective o_1 . The focal plane of the monochromator objective, in which the two superimposed spectra are contained, coincides with the fixed slit s of the actual spectrophotometer. The spectrophotometer part consists of the slit s , the collimator k_2 , the prism p_2 , the objective o_2 , and the ocular slit a . A sharp image of the slit s and the two spectra figured upon it by means of the monochromator is formed in the ocular slit. The images of these spectra are now super-

imposed upon one another by the aid of the twin prism z (Figure 3) at the objective o_2 , so that only a single image is seen in the ocular slit. By the aid of this construction, which has often been applied in photometric instruments, the separate rays which are produced by the double lens o_1 , are brought together again so that the observer upon looking into the ocular slit sees the upper part of the twin prism z in the light which comes from the lower part of the double lens o_1 , while the lower part of the twin prism z is illuminated by the light coming from the upper part of the double lens o_1 . If a coloured substance is now placed in the upper ray of light and an arrangement for weakening the light (in this case a grey wedge) is placed in the lower ray, then both parts of the twin prism z can be uniformly illuminated by weakening the lower ray.

The prisms p_1 and p_2 are each connected with a lever h_1 and h_2 by the action of which the monochromator and the spectrophotometer can be adjusted to the spectral field chosen.

The construction of the apparatus is greatly simplified by its division into two parts at the line $A-B$ which are closed together like an open book. Two reflecting prisms of 90° are fixed at the point of intersection which deflect the light ray twice. By this means the axis of the prism p_1 lies exactly upon the axis of the prism p_2 and the levers h_1 and h_2 coincide. Thus the monochromator prism is automatically coupled with the photometer prism. The movement of the now single lever causes such a change of position of the two small spectra at the slit s that the colour placed in the monochromator continually appears in the ocular slit a of the photometer. This device therefore entirely does away with the wearisome fresh adjustment of the monochromator to harmonize with the photometer.

The device for registering is comparatively simple. The movement of the lever h , which serves to adjust the spectrum field in the photometer, follows the curved path v (Figure 4). The curve is set in motion by toothed gearing t , the axle of which moves the registering table from left to right by means of rack and pinion drive. Thus when the spectral field is shifted by the milled screw n immediately before the observer, the paper placed upon the table moves in the direction of the abscissa with the speed accurately determined by the rack and pinion motion

and the form of the curve. If the table is divided from left to right into wave lengths, the prism can be adjusted according to every position of the table. It is even possible to convert the form of the spectrum which is very awkward for practical purposes and depends upon the quality of the glass used, into the uniform division of the bent spectrum.

The reduction in the strength of the one light ray, which is necessary to produce uni-

on and the colouring matter is laid in the upper part of the light ray of the monochromator at *m* (Figure 1). Coloured solutions are placed in a small tray *m*, well known in other connections, the lower part of which is filled with a piece of glass about 20 millimetres long (the so-called Schulz body). The observer keeps his left hand on the screw n_1 and his right hand on the screw n_2 , and by means of n_1 moves the table to the right as far as it can go, whereby the deepest red

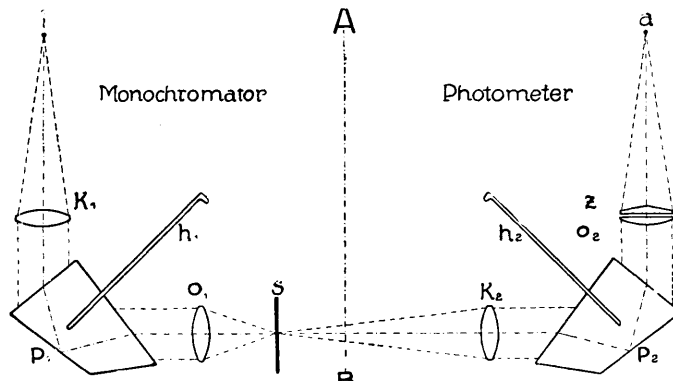


Fig. 2. Path of the rays seen from above.

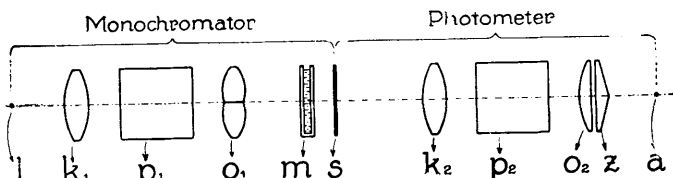


Fig. 3. Path of the rays from the side (opened bookways).

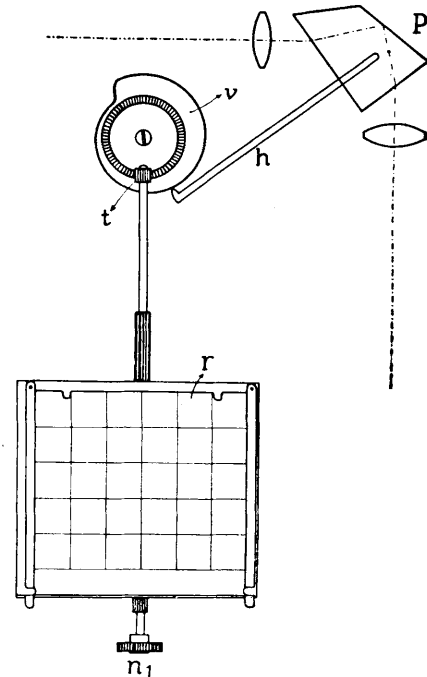


Fig. 4. Recording the wave lengths.

formity and in order to determine the absorption in the spectral field in question, is carried out, as mentioned above, by means of a grey wedge (cf. Figure 5). This motion is actuated by means of a rack and pinion set in motion by a milled screw n_2 . The rack is firmly connected with the registering table *r*, so that simultaneously with the movement of the wedge *d* the registering table and the graph sheet attached to it move downwards, i. e. in the direction of the ordinate.

A small pin *f* with a fine point is situated under the table (Figure 6) and can be lowered onto the paper by means of the lever *b* at the side of the apparatus. This causes a tiny prick in the paper which then forms the abscissa curve.

Measurements are carried out in the simplest way conceivable. The light is switched

appears automatically in the field of view. Uniformity in the field of view is adjusted by the screw n_2 . The lever *h* immediately above the screw n_2 is actuated without removing the right hand from the screw. The graph paper it thus automatically pricked at the ordinate corresponding to the red rays in the abscissa corresponding to the coefficient of extinction in question. Thereupon the screw n_1 is turned, keeping the field all the while in view, until a difference can be observed in the field of view, that is to say, until the coefficient of extinction has noticeably changed. Then the screw n_2 is moved a little till uniformity is secured again, a second prick is made, and so on (see Figure 7). This method of measurement and notation has at the same time the advantage of not having to make an unnecessarily large number of mea-

measurements at places where the abscissa curve flattens out.

The apparatus is as exact as the curves found in publications generally are, which is to say that it is accurate enough for all prac-

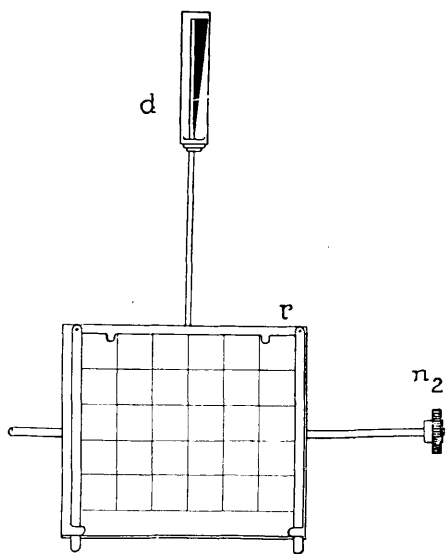


Fig. 5.

Recording the coefficient of absorption.

tical purposes. The wave lengths harmonize exactly to about from 2—3 $\mu\mu$. The extinction coefficients are accurate to about 0.05 in logarithmic units. The thickness of the curve shown in Figure 7 meets the accuracy required by the instrument.

A very important field of observation, but one which has hitherto been neglected, is the

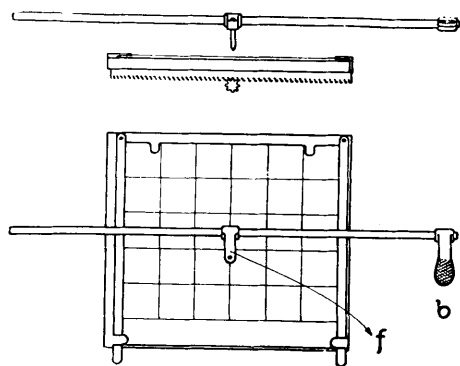


Fig. 6. Record pin.

determination of the absorption curves of colourations on paper, fabric, and so on, for which purpose the colouring matters are chiefly used in practice. Apparatus are hardly

even known which can carry out such simple measurements, but the spectrodensograph permits of this being done very easily. Part of the light from the arc lamp is thrown by means of the lens *e* and the mirror *g* (Figure 8) upon the coloured body *u* to be examined which has been fastened at an angle of 45° to the axis of the apparatus. The spot of light must then occupy the position of the upper spectrum of the monochromator. The underpart of the photometrical field of view is thereby illuminated by the light from the coloured body to be examined, while the up-

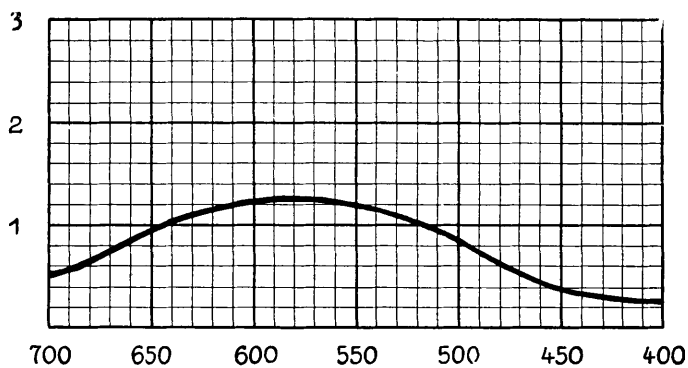


Fig. 7.

per part still receives light directly from the arc lamp. By inducing equilibrium in the field of view, as described above, the curve is automatically registered upon the graph

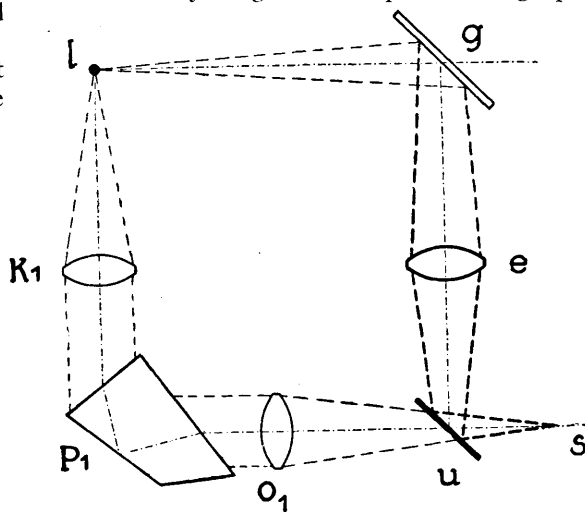


Fig. 8. Illumination from above.

paper. Of course the information given by this curve no longer corresponds to the normal extinction coefficient. In order to reach zero, a piece of white paper must be

inserted instead of the coloured body before or after the tests and the zero line settled by inducing equilibrium in the photometric field of view.

To sum up, the spectrodensograph possesses the following properties:

1. By its means there can be determined the absorption curves of liquid and solid transparent coloured bodies of a thickness up to 30 millimetres, as well as of solid non-transparent coloured bodies such as paper, fabric, etc.

2. Measurements are made in the dark, so that the eye is not disturbed by reading off.

3. The curve is produced automatically during the measurements and does not need to be calculated and plotted.

4. With the aid of the spectrodensograph a curve can be determined in from two to three minutes as against the hours hitherto found necessary.

5. Reflexions such as occur in the ordinary spectrophotometers, which make measurements in the dark parts of the spectrum illusory, are here eliminated by the automatic adjustment of the monochromator.

6. The absorption curves can be determined by totally unskilled personnel.

Palatine Fast Colours in Wool Dyeing

By Dr. *Nüsslein*

Some considerable time has passed since the conception of colour fastness could be brought home to the broad masses of the public. Notwithstanding initial difficulties and a great variety of handicaps which stood in the way of progress, there is today no longer any doubt as to the advantages — whether economic or aesthetic — derived by the wearer of a fast-dyed piece of clothing. It is an established fact that fastness of colour is beginning to be appreciated and that by and by the public will be fully alive to its importance.

Matters, in our opinion, are least complicated in the industry consuming cotton and similar fibres, where thanks to the inventive mind and practical collaboration manufacturer and consumer are in a position to comply in a far-reaching manner with their mutual requirements. It is not so in the woollen industry. Looking for reasons, we could find a great number. Not the least of them is the fact that a much longer time ago the wool industry could already boast a comparatively great number of very good dyestuffs, some of which are of importance even today. The conception of fastness which was long considered to be indissolubly bound up with the dyeing of the wool in the loose state had its origin in this very time. The description of "wool-dyed" as denoting colour fastness did not begin to lose in importance until the chrome developing dyestuffs were introduced also in piece-dyeing, where their advantages were ever more appreciated.

For many years the colour works have been placing such dyestuffs on the market which, whilst allowing to be dyed on piece-

goods in a comparatively simple manner, possessed very good fastness. New economic considerations, however, which since the beginning of the 19th century came more and more to the fore, resulted in the demand for a very cheap and simple method of dyeing. These demands were met before all by the acid dyeing colours. Their method of application and the possibility of producing goods of excellent appearance in a most simple manner, in addition to price considerations, caused them to be adopted on a broad basis. There can be no doubt that not every woollen article must be fast, and it is just as certain that today there are available a great many acid colours which satisfy ordinary demands in respect to fastness. Some of the representatives of this class even possess excellent fastness to light. But the regrettable fact remains that many articles which, considering the value of the material they are made of, should never have been produced with any but fast dyestuffs, are dyed with cheap colouring matters of unsatisfactory fastness.

It would be going too far here to enter into the relations of fastness on the one hand and manufacturers, traders and consumers on the other.

As already mentioned, the chrome developing dyestuffs before all are for us the representatives of the fastest dyestuffs and the acid colours the products most easily to apply. It is an old problem to combine the fastness of one class with the simple method of application of the other.

A group of dyestuffs has been available for some time which answers these requirements. The Palatine Fast Colours, under which name

these dyestuffs have been grouped, are chrome developing dyestuffs in character, but acid colours in their method of dyeing. The formation of the lake, which otherwise takes place on the fibre, is already accomplished in the course of manufacture. Dyeing is carried out with the addition of sulphuric acid, though as regards the quantity required for the production of a satisfactory shade, the Palatine Fast Colours differ from the acid colours. Fears entertained at the outset in certain quarters in respect of detrimental effects on material and apparatus have not materialised. Even when employing 8—10% sulphuric acid the quality of the pieces dyed with Palatine Fast Colours is considered very good, sometimes even better than of goods dyed according to the customary method. The quantities of acid indicated are required for fully developing the fastness and body of shade. In dyeing the Palatine Fast Colours differ very considerably from the acid dyeing products by Glauber's salt bringing about a diminution of the levelling property, so that the dyestuffs are best dyed without this levelling agent so important in wool dyeing. This method of dyeing may strike the practical man as a little odd, but nevertheless beautiful and excellently level results will be obtained with Palatine Fast Colours also under different conditions, and even on carbonised, non-neutralised goods. There can be no doubt that many practical men will be slow in grasping this fact, as it is altogether incompatible with former wont and practice. But to be progressive it is necessary to revise one's views from time to time and not to be prejudiced by antiquated notions.

The duration of dyeing when working with Palatine Fast Colours somewhat exceeds the time required for acid colours. If it is remembered, however, that the advantages derived from this class of dyestuffs are very considerable indeed, this will not be found to matter. The art of shading, which is not quite so easy with these dyestuffs as hitherto, may be acquired. As proved by dozens of cases in practice no difficulties are to be anticipated on that score after a few trials.

The new dyestuffs are valuable not only because they fulfil the demands made by manufacturers in such a high degree, but before all because the wearer of goods produced with Palatine Fast Colours can be convinced that they really answer his requirements in respect of fastness. The Palatine Fast Colours possess fastness to light, washing and water,

perspiration and atmospherical conditions in a degree as we used to expect of chrome developing dyestuffs only, but which we look for in vain in the case of acid colours.

The good fastness properties are an indication of what articles should be dyed with Palatine Fast Colours. Gentlemen's suitings come before all into consideration. Though many quarters have come to the conclusion that apart from chrome developing dyestuffs the Palatine Fast Colours are the only products admissible for better class goods, combinations of ordinary acid dyeing colours are nevertheless much in use, notwithstanding the fact that the fastness obtained frequently falls far short of that which it is the buyer's right to expect. Similar conditions are obtaining in the manufacture of ladies' better class costume cloths, rain coat materials etc. It is just wearing apparel of good resistance to atmospheric conditions for which the Palatine Fast Colours are excellently adapted. Even goods containing cotton may be dyed satisfactorily with these products without the risk of a perceptible injury in consequence of the amount of sulphuric acid used, provided the goods are thoroughly rinsed after dyeing.

They are just as well adapted for union linings, on which the most exacting demands in respect of fastness to perspiration are necessarily made, as for all-wool goods. Their application for articles containing cotton which has been dyed with sulphur dyestuffs is, however, deprecated.

Owing to their fastness the dyestuffs are of course also recommended for dyeing weaving and knitting yarns intended for hosiery and similar goods. Their fastness to washing and perspiration is of greatest importance in this instance.

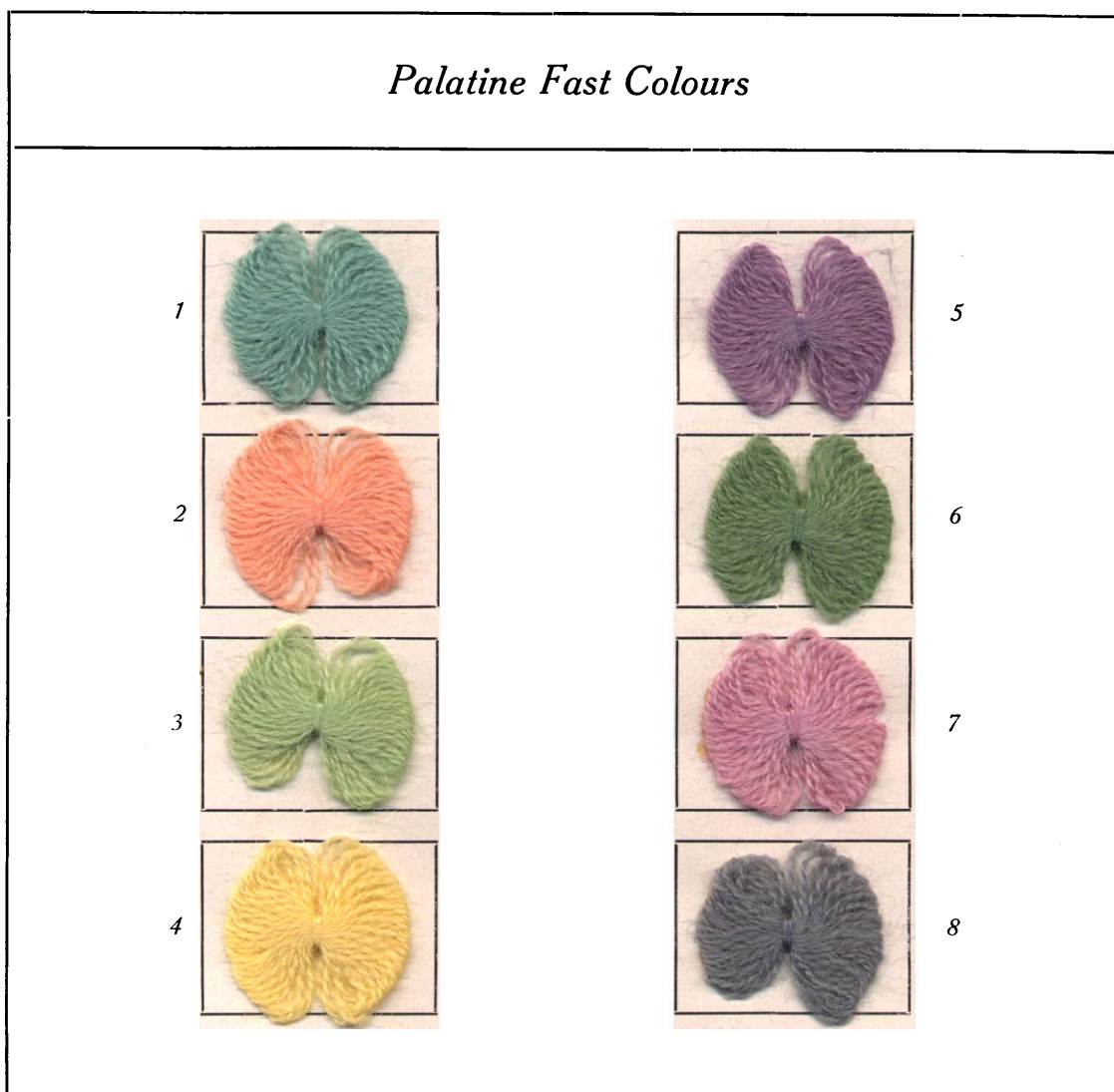
The Palatine Fast Colours may also be used for dyeing loose wool and slubbing. The number of products satisfying the requirements of a very severe milling as is essential for military cloths etc. being, however, still limited, they cannot come into consideration for such purposes generally.

It is to be expected that colour manufacturers, before all the I. G. Farbenindustrie Aktiengesellschaft will find ways and means to produce in the course of time dyestuffs answering these requirements.

The progress made by chemists in this new dyestuff production during the last two years holds out hopes for such object being attained. The originally very meagre range has

been enlarged by the I. G. to such an extent as has not been equalled in the same space of time by any other class of dyestuffs. A wide range of shades may now be produced with Palatine Fast Colours, though the brightness of many acid colours is not attained. In this respect the situation is very much the same as in the case of the chrome developing dyes

stuffs, we are, however, in a position to satisfy the most important requirements. Especially for the production of the so-called mode shades on piece and yarn a whole series of dyestuffs is available which in suitable combinations must without fail lead to the desired result, if working is carried out in a proper manner.



1. 0,1 % Palatine Fast Green BL conc.
2. 0,05 % Palatine Fast Orange GN
0,03 % " " Pink B
3. 0,03 % Palatine Fast Green BL conc.
0,23 % " " Yellow 3GN
4. 0,04 % Palatine Fast Yellow GR
5. 0,11 % Palatine Fast Pink B
0,025% " " Orange GN

6. 0,1 % Palatine Fast Blue GR
0,15 % Palatine Fast Green BL conc.
0,08 % " " Orange GN
0,04 % " " Yellow GR
7. 0,15 % Palatine Fast Pink B
0,035% " " Blue GG
8. 0,22 % Palatine Fast Blue GR
0,1 % " " Orange GN

It is possible that in certain cases the cost of the products will be considered too high, but it will, as with others, be only a question of time when it will be possible to make reductions in price. But even under present circumstances, the fact that the value of the dyestuffs justifies their cost should not be

lost sight of. The satisfaction at the smooth course of manufacture coupled with the savings effected by avoiding faulty goods and claims are not to be underrated. Another point is that material leaving the dyehouse "palatine fast dyed" is sure to answer all fastness requirements of its wearer.

Stable Diazo Printing Colours and a New Explanation of the Constitution of Diazo Compounds

By Dr. *W. Sieber*

Communication from the Research Institute for the Textile Industry in Reichenberg. Paper read at the Twelfth Congress of the International Society of Chemists and Colourists in Carlsbad.

The attempts which have hitherto been made known to replace acetic acid in the diazo printing colours for the beta-naphthol prepare have not been completely successful. As is well known the acetic acid arises from the sodium acetate which is added as a saturating or neutralizing agent for the mineral acid (hydrochloric acid or sulphuric acid) employed.

It is impossible to print the diazo colours containing sulphuric acid, hydrochloric, or phosphoric acid, because of their action on the fibre and also on account of the back greys. Diazo colours which are kept more strongly acid by the acids mentioned do not couple sufficiently.

The acetates of the diazo colours, however, decompose easily, and other organic acids such as formic acid, tartaric acid, citric acid, and oxalic acid act at least no better than acetic acid. The search for a suitable substitute for acetic acid in diazo printing colours has occupied the attention of the colourists of printing establishments and colour works for a long time. I myself took up the problem and found in 1906 that certain mineral acids which do not attack the fibre can very well replace acetic acid, for instance boric acid and tungstic acid.

If boric acid, in the form of commercial boric acid anhydride, is dissolved in hydrochloric acid diazo solutions after they have been neutralized with an excess of calcium carbonate (used in the form of whitening), these solutions and the printing pastes prepared from them can be kept for several days without decomposing or weakening.

If a solution of borax is carefully added directly to hydrochloric acid diazo solutions,

even when cooling, as is done with sodium acetate, the solution froths and decomposition sets in. That is to say, the neutralization of the hydrochloric acid diazo solution beforehand with calcium carbonate cannot be dispensed with.

When tungstic acid is used, it is not necessary to neutralize the solution before adding it in the form of a solution of sodium tungstate. The addition of tungstic acid has proved to be particularly advantageous in the case of p-nitro-o-anisidine red, especially when pink shades are to be printed. Even colours that have been let down as much as 1:24 give clear shades and even these light shades last well.

Pink shades from p-nitro-o-anisidine have a bluish tinge which is much liked, while p-nitraniline red which has been let down becomes yellowish.

Diazo solutions which have been neutralized with calcium carbonate keep better, even in summer, without ice, perhaps even better indeed than the printing colours prepared with the addition of boric acid or tungstic acid.

The use of the acids just mentioned of course is more expensive and it need hardly be specially mentioned that stable diazo printing colours prepared with their aid are more particularly suitable for small prints and as part of multiple colour effects. That is to say, their use is advantageous when not much colour is required, when fresh colour is not often added, and the decomposition of the acetic acid colour soon makes itself noticeable. With heavy prints, on the contrary, where the printing colour must often be freshened up by the addition of more colour, it will be found that the acetic acid colour

will be sufficient. The recipe for the preparation of the stable diazo colours is as follows:

1. 500 grams Base (p-nitraniline, m-nitraniline, or p-nitro-o-anisidine) are made into a paste with
 - 1000 „ boiling water and then
 - 1000 „ hydrochloric acid 19° Bé are added. After having allowed to cool,
 - 3200 „ ice are added and then, all at once,
 - 325 „ nitrite (whereby the temperature sinks to — 5° C). When diazotization is complete, add slowly
 - 500 „ calcium carbonate. After stirring, filtering, and washing
 - 180—240 „ boric acid are added to the filtrate.

The whole is made up to 10 kilos and thickened with 15 kilos gum tragacanth or neutral starch thickening.

2. 500 grams Base are diazotized as directed above.

After diazotizing, neither chalk nor boric acid is added, but a cold solution of 600 grams sodium tungstate in 1200 grams water.

When the diazo compounds are coupled with naphthol on the fibre, the diazo solution should be slightly acid or weakly alkaline; the processes hitherto known all use weakly acid solutions. If treated in the usual way, the diazo solution contains sodium acetate besides free acetic acid.

At a temperature of 25° C acetic acid has the dissociation constant of 1.86×10^{-5} and the acid exponent of 4.73. The presence of sodium acetate reduces the dissociation of the acetic acid and the acid exponent therefore naturally counts higher, that is to say, the acidity becomes less. Boric acid at the same temperature has a dissociation constant of 6.6×10^{-10} , the acid exponent is 9.18. Tungstic acid is an ampholyte with mainly acid properties, and as an ampholyte can only be a weak acid. I was unable to find from the literature the dissociation constant and the acid exponent of tungstic acid, so that I cannot even say whether these constants have already been determined.

It is evident from these figures why boric acid and tungstic acid have proved be suitable for use in coupling the diazo compounds with naphthol. They are weak acids. In passing it may be remarked that the degree to which

cellulose fibre is injured depends upon the dissociation capacity of the acids, that is to say, the dissociation constants are a measure of the power to injure textile fibre.

Both boric acid and tungstic acid are weaker acids than acetic acid and they can therefore have a more favourable action than the latter. The dissociation constants and the acid exponents of a number of organic acids at 25° C may be tabulated as follows:

oxalic acid	dissoc. const.	3.8×10^{-2}	acid expon.	1.42
tartaric acid	„	9.7×10^{-4}	„	3.01
citric acid	„	8.2×10^{-4}	„	3.09
formic acid	„	2.05×10^{-4}	„	3.69
lactic acid	„	1.55×10^{-4}	„	3.81

Experience has showed that they act more unfavourably on the coupling. (The constants given are taken from J. M. Kolthoff, „Der Gebrauch von Farbenindikatoren“.) When a diazo solution which contains weak acid and also sodium is brought together with the alkaline naphthol prepare it may be supposed that the free alkali of the naphthol prepare acetate is first of all saturated with acetic acid and that the formation of the azo colour proceeds only in the presence of sodium acetate. That would accord with the usual method of working in the manufacture of azo colours when the dyestuffs themselves are actually prepared and not on the fibre, namely coupling with phenols in the presence of a weak alkali. When the diazo solution contains boric acid there are formed under corresponding conditions quite evidently an alkaline borate with an alkaline reaction, and with tungstic acid a weakly alkaline tungstate.

After what has been said there is no need to go further into an explanation of why the stronger acids, such as oxalic acid, tartaric acid, citric acid, formic acid, lactic acid, are less favourable for the formation of the azo colouring matter. It will also be evident why aluminium sulphate, which is used especially in the diazo solution prepared from Fast Red GL Base (Griesheim), can exert the desired favourable action upon the coupling owing to its reaction not being strongly acid. Furthermore it is clear why the formation of an azo colouring matter takes place so smoothly with the use of a neutral diazo solution and a naphthol prepare which contains potassium carbonate and much ricinoleic acid. (I reported upon the process on the Congress last year in Dresden.)

The electrochemical constants cited are only comparatively of value, because the con-

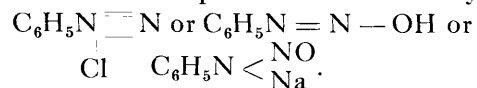
ditions are probably much less simple owing, in particular, to the presence of the diazo compounds or of the components, as has hitherto been supposed, of the diazo compounds. At all events, it can be concluded that acids, the dissociation capacity of which is greater than that of acetic acid, are liable to influence the coupling process less favourably.

These constants evidently influence also the stability of the diazo solutions, for such solutions containing boric acid and tungstic acid are more stable than those with acetic acid, while the neutral solutions are still more stable.

Among the letters which the „Chemiker Zeitung“ published in the Jubilee number of December 29, 1926, on the occasion of its half centenary, is the following communication from R. Wegscheider, of Vienna: “The progress of science is not entirely due to treatises and patents which are or at least should be based upon carefully carried out experiments and deliberations. Suggestions too must not be undervalued which proceed from casual expressions of opinion and chance observations”.

I have these words of Wegscheider's in mind when I communicate to a wider circle of technical colleagues the views which I have formed upon diazo compounds for the most part already more than twenty years ago in consequence of and on the basis of intensive study of the formation of azo colours upon the fibre. These studies would appear to find confirmation in recent investigations, I would mention in particular researches upon molecular compounds, especially organic molecular compounds, and in the changed perceptions gained in this way.

According to the current view, diazo compounds have a composition either of the type



One form can be changed into the other according to the conditions of reaction.

The diazo compounds are supposed to originate in the following way. One molecule of water separates out of one molecule of primary aromatic amino salt and one molecule nitrous acid:



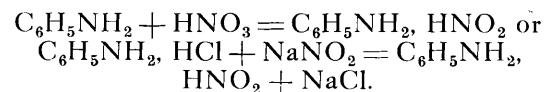
which implies a condensation process. Condensations appear in general at high temperatures, or by the action of agents which have a strong tendency to extract water, or under

the influence of both of these factors. Neither of them is present in the formation of aqueous diazo solutions which takes place at a low temperature, in so far as the production of azo colours on textile fibre comes into consideration, and no condensation agent is present.

The aqueous solutions of diazo compounds behave under the influence of heat like a solution of ammonium nitrite, which decomposes into free nitrogen and water, while diazo compounds form free nitrogen and phenols.

The formulae of diazo compounds given contain three or even four bonds of the nitrogen atoms. V. Meyer, in „Ergebnisse und Ziele der stereochemischen Forschung“, published in 1890, has shown that ethylene compounds are generally formed at high temperatures. I have not been able to find out whether such conditions have been experimentally proved also for organic nitrogen compounds containing multiple linked nitrogen atoms, but there is a presumption that this is the case. The origin of double links according to the usual explanation of the formation of diazo compounds is closely united to a condensation process, since water is split off. This would be explicable if a compound were formed which was insoluble in water, but this is not so. The product formed by the action of nitrous acid upon aromatic amino bodies in the presence of water remains dissolved in water. According to the modern theory, when chemical compounds are dissolved in water, an addition of water first takes place, that is, the formation of a hydrate. It cannot be seen why water should be split off into the water of solution upon the formation of the reaction product of an amino compound and nitrous acid.

The conviction simply forces itself upon the mind that the reaction of amino body and nitrous acid in aqueous solution is, at least first of all, an accumulative reaction. The process in a strongly cooled aqueous solution would probably be that shown by the equation

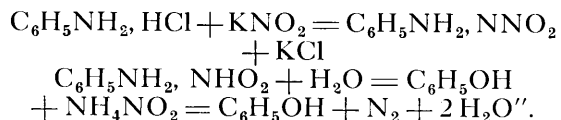


As a matter of fact the action of nitrous acid upon p-nitraniline chlorhydrate without any excess of hydrochloric acid produces at once a diazo compound, as I have shown in my remarks in the article „Anwendung von Kaliumverbindungen in der Druckereipraxis“ (Melliand Textilberichte, 1926, page 615) and

in my paper read before the Congress in Dresden. If an excess of hydrochloric acid is present a labile state of equilibrium arises.

When nitrite is entered into suitable diluted, strongly cooled hydrochloric acid, the nitrous acid set free remains in solution.

That views similar to my own were held long ago is shown by the following passage in Beilstein's „Handbuch der organischen Chemie“, third edition, vol. 1, page 92, with reference to the action of nitrites: “Alkaline nitrites are used in all cases where a definite quantity of nitrous acid is required which must not be exceeded. In order to prepare, for instance, phenols from aniline and its homologues, the hydrochloric acid salts of these bases are treated with (1 molecule) alkali nitrite and then boiled:



There is no hint as to the observations upon which Beilstein based his reaction formula. Here, therefore, in the preparation of phenols from amino bodies and nitrous acid, a diazo compound is not mentioned as intermediate product, but aniline nitrite.

P. Pfeiffer, in „Organische Molekülverbindungen“, page 27, remarks: “One advantage of the coordination theory formulae over the pure valency formulae is, I should say, that in them the components are simply laid close to one another by mutual saturation of affinity, without atoms being separated which were formerly united. *Separations of atoms and transformations should only be assumed when that is absolutely necessary, because otherwise unfruitful speculations arise and undermine the foundations of all determinations of constitution*”. In the reaction amino compound + nitrous acid = nitrite of amino compound, the nitrosamines (Schraube and Schmitt) do not require the constrained explanation of a transplacement if it is assumed that there are accumulation compounds of nitrite at the amino body, the choice being left free to regard nitrite as being constituted according to the scheme NOONa or NaNO_2 .

According to Banchard, nitrous acid at a temperature of 25° C has a dissociation constant of 4×10^4 and an acid exponent of 3.40, so that it is a stronger acid than acetic acid. It will therefore be understood that acetic acid and the still weaker acids do not decompose the nitrite amino compounds and that

azo dyes therefore are produced on the fibre in the presence of weaker acids than nitrous acid, and also why the coupling is either at least incomplete, or does not occur at all, when stronger acids are present. It is well known that no azo dye is formed if an excess of strong acids is present.

The explanation of the origin of azo dye-stuffs from nitrous acid compounds of amino bodies is unconstrained.

There are a number of organic molecular compounds, i. e. accumulation compounds, the origin of which can be compared with the formation of the nitrous acid compounds of amino bodies.

If, however, the classical formula of the diazo compounds is regarded as being correct, then the nitrous acid amino body must be looked upon as an intermediate product. Analogies for the formation of intermediate products, molecular compounds, can be found in considering substitution processes, whereby only those of the aromatic series should be taken for comparison.

In a few cases (for details see P. Pfeiffer, „Organische Molekülverbindungen“, page 264 et seq.) it could be directly proved that an additive process precedes the substitution process in halogen substitutions, by isolation of the primary molecular compound.

In the nitration of aromatic amines (cf. P. Pfeiffer, loc. cit. page 272) a nitrate is first formed which is transformed into a nitranilide under the influence of an agent which splits off water, the nitranilide transforming itself to amines nitrated in the nucleus. (I refer in this connection to my remarks upon reactions of condensation.) The sulphonation of aromatic amines (cf. P. Pfeiffer, loc. cit., page 272) proceeds quite according to the scheme of the nitration. If aniline is treated with concentrated sulphuric acid, there is formed first of all acid aniline sulphate which, according to Bamberger, is transformed into phenylsulphaminic acid by splitting off water. This sulphaminic acid is converted by treatment with dilute sulphuric acid into the *o*-sulphonic acid of aniline, and by treatment with concentrated sulphuric acid at a raised temperature isomerized into *p*-aniline-sulphonic acid. (That is to say, here too a condensation process sets in only after the use of an agent which removes water, at the same time raising the temperature.) The scope of a lecture which should be kept as short as possible makes it impossible to go into details minutely, but even without this it may be

assumed that the origin of nitrous acid amido bodies by the action of nitrous acid in aqueous solution upon primary amino compounds is, at the lowest, very probable.

About twenty years ago I withdrew myself

from chemistry, but the occurrences of recent times have induced me to resume my chemical studies. Certain extraneous conditions have, however, prevented me from continuing my work upon the subject under discussion.

An Important Advance in the Dyeing of Artificial Silk

By *W. Alterhoff*

Artificial Silk has scored a huge success!—All statistics prove the astonishing increase in the manufacture and the consumption of Artificial Silk. Therefore many concerns dealing with this yarn have tried to work on more economical lines, yet giving a greater production. As real silk has lost some of its former standing on the market, owing to the increasing demand for Artificial Silk Dyers have more or less been compelled to find a good and quick method for treating this yarn in order to cope with this increasing demand of the market, and with improvements as regards quality. For these reasons the Dyer must keep himself informed with all latest developments regarding the various classes of Artificial Silk yarns. With its adaptability for all possible purposes this yarn has a very bright outlook for the future, with the opening of new markets.

A special difficulty in the treatment of Artificial Silk is the unevenness of the dyeing, so often deplored by experts, this difficulty is caused, as is generally known, partly because of the nature of the fibre, being an artificial product, and therefore cannot replace the natural product in every case; there are further some dye-technical reasons such as the great affinity of Artificial Silk for the dyestuffs; a false application of the bath; too great an addition of Glauber's Salts; an insufficient cleaning of the cistern before dyeing, etc. A very important point is the regularity of the treatment of the yarn in the dyebath, it is therefore not astonishing to find that machine dyeing has been coming more into use for the Artificial Silk yarns. Messrs. *Tillmann Gerber Söhne & Gebr. Wansleben, Krefeld*, have increased the range of available machines with a new Patent machine, and it is a very valuable link for the future.

The difference between this new Spray Dyeing Machine and those at present in use, is that the skeins hanging on the rollers are not only immersed in the dye liquor, but are simultaneously sprayed from both inside and outside with the liquor through suitable spray pipes specially arranged, as in the case

of a skein washing machine. As the machine has also water connections, the skeins can be washed and brightened immediately after having been dyed, simply by pumping off the dye liquor to a reserve cistern, and running in a special warm bath, without any unloading of the skeins being necessary.

The writer of these lines has seen these machines at work in one of the largest artificial silk dyehouses in Germany, and would like to give a short description of the method of working. The machine in question was of the large type, dyeing simultaneously approximately 100 kilos of yarn. During the preparation of a warm bath of about 50—60° C with an addition of 2% Monopol Soap, the Skeins were hung on the rollers, which were then hydraulically lowered, and run through the bath until thoroughly wetted out. Then the rollers are hydraulically raised again and the bath heated up, by a new boiling device which is fitted to the bottom of the cistern, no steam coils being necessary, then the dyestuff was added. This new boiling system produces in the shortest possible time an absolutely faultless and even dyebath, in spite of the fact that the dyestuff was added direct to the bath in a dry form.

The yarn under treatment had to be dyed in a fashionable shade to sample; throughout the whole process the machine only required the attention of one man, and although it was a difficult shade to dye, the goods were finished in three quarters of an hour, with, in this case, three additions of dyestuff until the required shade was obtained, the results being perfect in every respect. This short time was not only due to the regular movements of the rollers, but also mainly due to the spraying mechanism by which the skeins were intensively and evenly sprayed, the dyestuff penetrating through the fibres. The dyeing process being finished, and the dyestuff having been drawn off by pumps, the skeins were rinsed and brightened in a luke warm bath containing a certain percentage of Formic acid and some Oil emulsion. The same weight of yarn, when processed in

the usual everyday method, requires not only more men but three or four times more time, the process being much longer until the shade is matched, and the yarn is ready for the Shaking Machine or the Drying Room.

A further advantage of the machine is that the skeins remain evenly laid out on the rollers during the whole process, there being no tendency for the yarn to creep to the flanges of the rollers, as in the normal type of dyeing machine, thus requiring a good deal of extra attention. A further point to note is that the Cisterns are lined with Porcelain Plates, which are perfectly smooth, and are easily and quickly cleaned out ready for the next shade. It is further possible to place above the machine a reservoir to contain a dyestuff that has been used, which is too valuable to

be run away to waste, for example a Black can be stored for later use. The three sizes of roller groups, at present built, can be combined in any way, according to the desired production.

It cannot be denied that the advent of this machine will cause a change in many works, where more efficient and quicker treatment of the yarn is desired, and one must also acknowledge that the machine is built in a good solid construction with the finest possible workmanship.

Several critics of the Spray dyeing method, having seen these machines working, have had to confess that the results were astounding, it is said that success crowns work, and in this case there is no doubt that Messrs. Gerber's will reap the benefit from the successes of their machine.

The Sizing of Artificial Silk

By *H. Svarovsky*

Nitro, acetate, viscose, and cuprammonium silk are used for weaving, all of them products which A. Rosenberg correctly terms long fibres and which have faults more or less, that make them unsatisfactory for this purpose. On its way to the loom this still imperfect textile fibre is subjected to strain in winding, warping, beaming, and sizing. For coloured goods the yarn is sized in the hank, which has the advantage that there is less loss in winding and beaming on the cone winding machine, than when working with unsized yarn for the sizing machine. If there is not much yarn to be dealt with, it can be passed by hand through the size, but if any large quantity is being worked up it is advisable to use an automatic sizing machine with from 4 to 6 rollers, or a machine with two rollers. This mechanical treatment is not so hard on the fibres and machines of this type have recently been constructed with conspicuous success. Warps of from 10 to 30,000 yards in length are sized from the beams on the air-drying sizing machine. A number of sizing and also air-drying machines of the old type have the fault that gelatine sizes and the other sizes on the market do not penetrate the yarn perfectly, which is due partly to the nature of these products, partly to the yarn being run too rapidly through the machine, so that the sizing material on the thread falls off to some extent after drying and when being woven. Goods of this kind show in places even after finishing glossy and rough patches,

and a German and a Swiss machine works which have made a speciality of this field have built a particularly suitable air-drying sizing machine without fans which does away with these faults. Other steps also can be taken such as taking particular care in preparing the size, a point that applies to the sizing of other textile fibres also. There are still a great many weaving mills that do not have their sizing done properly by the use of practically tested and simple means, although this is one of the most important preparatory operations. Without regard to the nature of the textile fibre to be sized, it can be said that alterations intended to improve the sizing fail owing to the management often being loath to give up old methods. In many works the weaving sheds look like a flour mill and most of the starch is on and under the looms. The reason of this is that the size in the sowbox is continually kept at the boil, and if besides this there is direct steam in the box the starch and the other additions to the size will all the sooner become unusable.

The equipment necessary consists of a boiling vat of soft wood holding from 300 to 400 litres, fitted with a measuring rod showing the content from 10 to 400 litres by 10 litres at a time, a copper heating worm, indirect steam, a stirrer with 120 r. p. m., a three-inch outlet tap, fitted either on the bottom or at the lowest part of the vat in such a way that the contents can completely run off. The vat must be easy to clean and rinse out and must

be so high that an enamelled pail of 15 litres content can be set under the tap. For use with a number of sizing machines, larger vats must be employed, from which the size is led through pipes to the size troughs. Besides this three or four enamelled pails holding 15 litres, a fine sieve of brass wire, and a thermometer are also required.

None of the various preparations now on the market should be used for the preparation of a really good size, for not many of them are of any value. When different products are mixed together and allowed to stand for some time, the size is inclined to decompose and one or other of the components is rendered inactive, so that it is of advantage to purchase the very best material and mix and boil it just before use. Such basic products are farina, wheat starch, dextrin, and water-soluble oil. The starch granules must be completely broken up before being boiled, for which purpose only a high-grade diastase is suitable. This statement is not to be regarded as an advertisement for the product, but practical tests extending over years have demonstrated that Diastafor is much superior to other sizing and desizing agents, ferments, and the like. The fibre is protected and the colours are brighter. *Starch is broken up in the following way.* Farina is dissolved in cold water, dextrin and Diastafor in lukewarm water. These mixtures are added to the vat through a sieve and heated to from 55—60° C, then the steam is shut off for 10 minutes. Other additions, such as oil and weighting agents, are also added through a sieve, avoiding alkalis, and then the whole is boiled till ready. A size prepared in this way must not be boiled any more during use, but simply kept at about the temperature of the hand. Coloured and bleached yarn should even be sized at a lower temperature.

The various kinds of long fibres have been sized more or less successfully with all sorts of materials and compositions without having been able to please the weaver. Much practical experience is needed to size properly all the various types of nitro, acetate, viscose, and cuprammonium silk, because the

material, coming as it does from different artificial silk mills, is not always of the same composition. One and the same size cannot be used for all long fibre yarns, but one must be chosen which is suited to the nature of the yarn to be sized, and this causes the sizer some difficulty, and trouble.

Twisted yarns are not always suitable for a fabric of good quality, and it is of great importance to use open weft yarn for the warp. Yarn which has been really well sized offers the weaver the advantage of a fabric with a better cover and a more pliable, softer handle than with twisted yarn, which is also more expensive. The weaver also wants the yarn after having been woven to have its original lustre and softness, and the colours must not be cloudy. It must be possible completely to desize goods which have been dyed in the piece and aftertreated. It has not yet been possible to produce an artificial silk yarn which could be woven perfectly after having been sized with preparations containing gelatine, ferments, and the like. This can readily be understood, because these products have not the property of penetrating the fibre thoroughly. As already mentioned, careful practical and scientific investigations have shown that Diastafor of a certain high capacity of a light colour is best suited to reduce the hygroscopicity of the long fibres and sizes them well by the action of the maltose together with a certain oil emulsion, so that it is practically impossible for the thread to become fuzzy. The thread can be made stiffer or more pliable just as the weaver would like to have it by properly regulating the additions made to the size.

The purpose of these lines is to give a few hints derived from practical experience upon the sizing of artificial silk, which is not yet perfectly understood. Practical tests will be further carried on in an experimental station in Vienna with all materials at disposal and with the assistance of high authorities in this field of investigation. Any inquiries will be answered and tests carried out with samples of yarn sent. The address may be had from the Editor.

How Should Artificial Silk Be Washed?

By Dr. L. Kirberger

Much uncertainty prevails about the washing of artificial silk and enormous damage has been done by its not having been properly handled in the wash.

Ignorance in this connection is, however, not confined to the consumer, but the consumer, the wholesaler, and even the manufacturer know much too little of the subject.

In the first place we will deal with those articles of clothing of artificial silk which must be washed owing to the way they are used.

The chief lines are probably knitted goods, Jersey cloth, warp loom and Milanese tricots, which are mainly employed for women's lingerie, underwear, and also for outer garments. For the most part they are made entirely of artificial silk, but also in admixture with wool or cotton.

Stockings and socks of artificial silk will hardly be found in the trade, tops, toes, and heels being for the most part made of cotton or mercerized cotton.

But what about woven under and outer garments? These too are very rarely made of artificial silk alone, but are generally woven in admixture with cotton, wool, or real silk. Fabrics composed of artificial silk with cotton or real silk are to be found on the market in the shape of men's shirts, drawers, pyjamas, lingerie, women's outer garments, and blouses.

The treatment of artificial silk in the wash is governed by its physical properties.

Everybody knows that cotton and linen fabrics can be treated pretty roughly in the wash, and they can be boiled, bleached, treated with hard soap on the washing board or in the washing machine, without suffering any serious injury.

It is quite a different matter with articles of clothing made of wool or even silk: they cannot be treated in this way.

No one would think of washing articles of crêpe de chine on the washing board or with a strong hard soap, because every housewife knows the properties of such fabrics and is well aware that silk or woollen articles must be treated very tenderly in the wash.

It is a step in the right direction when she takes similar precautions with articles of artificial silk.

Artificial silk, when dry, has a certain strength which is sufficient for all practical purposes, but it loses part of this strength when it becomes wet. Therefore articles of artificial silk must not be strongly wrung out, pulled, or rubbed.

It is smoother than any other fibre and consequently dirt does not cling to it very readily and penetrates only with difficulty into the thread.

Everyone who has worn artificial silk tricot underwear, especially of pure artificial silk, will himself have observed and praised this pleasant, unique property of artificial silk.

All types of artificial silk, with the exception of acetate silk, swell strongly, and thus tend to loosen any mechanical impurities attached to the fibre, so that they are removed without much mechanical treatment. For this reason, no fibre gets rid of dirt so easily when washed as does artificial silk.

When washed, it must not lose a fraction of its strength, nor its lustre or pliability. It is sensitive to the action of caustic alkalis, such as ammonia, caustic soda, and alkali, and also soda and sodium silicate, and can be made harsh and dull by the use of solutions of soap which contain considerable quantities of soda. It is quite possible to wash artificial silk properly with washing agents which contain slight quantities of bleaching agents, such as perborate, hydrogen peroxide, or hypochlorite, without injuring it.

The consumer, who is not acquainted with this state of affairs, will often complain about the washability of articles of artificial silk because the colour has run or has bled into other articles, and believes that the artificial silk is to blame.

Fully 85 per cent. of all artificial silk fabrics are dyed with loose colours, e. g. women's lingerie and stockings, single shade outer garments and blouses almost always, less often men's underwear and printed upper garments.

Goods of this nature should be washed at a temperature which the hand can just bear, i. e. at from 30—35° C (85—95° F).

Solid soap should not be used at all for artificial silk and it is advisable to employ one or other of the washing agents on the market, such as soap flakes or powder, and prepare soap solutions for washing artificial silk. Such washing agents must be cheap and have high cleansing power, and must be readily removed from the washed articles by rinsing.

A short analysis of the commonest washing agents on the market is given below together with a few remarks upon their suitability for washing artificial silk. The composition of Lux, Perflor, and Persil is as follows:

Lux	pure soap flakes
Perflor	85% soap 15% sodium perborate
Persil	42.5% soap 16.4% soda 9.2% sodium perborate 3% sodium silicate 28.9% water.

There can be no doubt that Lux is the least injurious, but the other two also cannot injure

artificial silk in the concentrations in which they are practically used at a temperature of from 30—35° Centigrade.

As is well known, the consumption of artificial silk is many times that of real silk. The whole trade takes an enormous interest in artificial silk and everybody who has to do with the fibre wants to explain about it, although his expert knowledge may be of the slightest. There have accordingly been presented to the public a number of instructions for washing artificial silk which were not always serviceable. For this reason several slight mistakes which have crept into these instructions are here corrected.

A well known manufacturer of washing agents recommends washing artificial silk in cold water.

That may be all very well when an artificial silk tricot which has been dyed with a loose colour is to be washed with a bleaching washing agent. If the fabric were only half artificial silk and dyed fast, it might even be boiled for a short time with a neutral solution of soap without suffering. Such a fabric would be difficult to wash clean in cold water.

The advice is often given to treat artificial silk after the soap solution has been rinsed out with a little vinegar to freshen up the colour. Artificial silk which had been dyed with dyestuffs used for dyeing cotton would thereby be stained and the fabric itself would be given a scroop, which is by no means always desirable.

It is just as unnecessary to wrap artificial silk, after rinsing it, in a cloth to squeeze it out; that can be done without the cloth.

Artificial silk stands ironing well and it

should be ironed as if it were real silk. Acetate silk is here too an exception and a fabric of this fibre must not be ironed too hot, which tends to injure it.

It is advisable to steep the artificial silk for about fifteen minutes in the washing liquor because, as already mentioned, part of the dirt is loosened of its own accord by reason of the peculiar physical property of the fibre.

Finally the following directions for washing artificial silk may be proposed here, which are briefly stated, but are intended to be of general application and also for fabrics which contain other fibres than artificial silk.

“Dissolve the washing agent (in the shape of flakes or powder) in water. Lay the articles in the solution for a short time and then wash them out at a low temperature. Strong wringing, pulling, or rubbing must be avoided. Immediately after having been washed rinse until the water is clear, and dry. The fabric stands ironing well. (Do not iron articles of acetate silk too hot.)

Articles of artificial silk and cotton that have been dyed fast can be washed warm with a washing liquor free from bleaching agents.”

If due attention is paid to the foregoing points, it is practically impossible that modern artificial silk should give rise to the least complaint about poor washability.

Every type of artificial silk can nowadays be washed, but it is only natural that certain special brands which show particular strength when dry and when wet have better washing qualities than ordinary viscose. But sufficient practical experiences have been gained which confirm that the latter also, whether woven or knitted, stands washing well.

The Dyeing of Acetate Silk

By Dr. *Rabe*

On account of its characteristic dyeing and physical properties acetate silk is an interesting and valuable addition to the number of available textile fibres. Like all kinds of artificial silk it is of vegetable origin, but is distinguished from other representatives of this class of fibres—cotton, ramie or the older varieties of artificial silk—by being an acetylated cellulose and not, like these, a regenerated cellulose. This difference in chemical composition is responsible for its entirely different dyeing properties and made it necessary to work out for acetate silk new dyeing and finishing processes.

Acetate silk, being an acetic acid compound of cellulose (acetyl cellulose), is very susceptible to all chemical processes involving saponification, i. e. splitting off of acetyl groups. Alkalis, specially at high temperatures, affect acetate silk to such an extent, owing to the saponification of the surface of the fibre, that the typical dyeing and other properties—lustre, tensile strength, solubility in acetone etc.—are completely lost. Acetate silk is sensitive to boiling water and steam, which is also due to its chemical character. It becomes dull and opaque and loses much of its tensile strength. The dyeing is therefore carried out

in baths which, as far as possible, are not alkaline and not too hot, the temperature being preferably not above 175° F.

Acetate silk is dyed in the form of yarn, pure acetate silk fabrics and mixed fabrics together with cotton, wool, silk or the other kinds of artificial silk. Hanks are dyed in the bark or on hank dyeing machines, piece-goods on the winch, the star-frame and on the jigger.

Cleansing. Goods which come direct from the manufacturer as a rule require only a preliminary wash as a preparation for dyeing. The case is different with worn goods which sometimes require to be cleaned only and frequently must also be re-dyed. A large number of stain-removing agents are available for the purpose of dry cleaning: pure organic solvents and preparations consisting of fat solvents with a base of soap or soap-like products. Great care must be exercised when these agents are applied to the cleaning of acetate silk, as many of them contain organic components which may dissolve acetate silk. No injurious effect is exercised on acetate silk, e. g. by ether, carbon tetrachloride, trichlorethylene, benzol, benzine, petrol ether and turpentine. On the other hand, methyl alcohol (Methanol), acetone, ethyl acetate and chloroform are very harmful, as they dissolve acetate silk even in the cold. Alcohol, acetic acid, amyl ester or chlorbenzol have some solvent action in the cold, but more at a higher temperature. On this account it is recommended to carry out preliminary trials with all detergents before they are applied to cleansing the whole piece and also because some acetate silk dyestuffs are soluble in these detergents, which only might make the trouble worse.

Preliminary washing. Before dyeing, the material is suitably washed. For this purpose a bath is prepared containing 3—5 lbs. Marseille soap and ½—1 pint concentrated ammonia per 100 gallons, the goods treated in it for about ½ hour at 100—110° F and rinsed thoroughly.

Bleaching. Acetate silk, as a rule, is a good white, and so bleaching before dyeing is not often required, but with mixed fabrics of cotton or wool it may be necessary. Two processes are employed for bleaching acetate silk: the permanganate and the hypochlorite of soda process.

The bath is prepared with 1—2 lbs. potassium permanganate and 1—2 pints concentrated sulphuric acid per 100 gallons. In this liquor the goods are treated for 1 hour at ordinary

temperature, rinsed and bleached in a fresh bath to which 2½—5 pints sodium bisulphite 72° Tw. and 1¼—2½ pints concentrated sulphuric acid have been added. The bleaching is finished in ½ hour. Subsequently the goods are rinsed thoroughly and, if desired, blued with a little Alizarine Irisol R, Alizarine Sky Blue B or Alizarine Supra Blue A. The hypochlorite of soda process is specially used for bleaching vegetable fibres in mixture with acetate silk. As acetate silk cannot be boiled off like cotton, being sensitive to boiling water, it is washed for 1 hour, at about 110° F, in a bath to which 3—5 lbs. soap, 1—2 lbs. Nekal BX dry and ½—1 pint concentrated ammonia per 100 gallons have been added. It is then rinsed and bleached for 1—1½ hours in a hypochlorite of soda solution containing 1—3 lbs. available chlorine per 100 gallons, rinsed again thoroughly, soured cold with 1—1½ pints hydrochloric acid per 100 gallons and rinsed once more.

Dyeing. After this preliminary treatment the goods are dyed.

The usual dyeing processes and — with a few exceptions — the ordinary dyestuffs cannot be employed for dyeing acetate silk. New dyestuffs and new dyeing processes had therefore to be invented. The following will be considered within the scope of this article:

1. Celloxane and Mordant for Acetate Silk for basic dyestuffs.
2. Cellit Fast dyestuffs.
3. Celliton and Celliton Fast dyestuffs.
4. Cellitazols.

Celloxane and Mordant for Acetate Silk. The basic dyestuffs have a certain affinity for acetate silk, but even from concentrated dye-baths only comparatively light shades can be obtained. With the aid of Celloxane and Mordant for Acetate Silk, however, it is easy to produce full dyeings with basic colours.

Celloxane is added to the hot (160° F) dye-bath containing the necessary dyestuff, best in several portions, according to the depth of shade desired. Dyeing is carried out in ¾—1 hour, the goods rinsed and finished as usual. The quantities of Celloxane required vary between 3—16 pints per 100 gallons.

The use of Mordant for Acetate Silk is similar to mordanting with Katanol O as practised in dyeing cotton with basic dyestuffs. The goods are treated for 15 minutes at 120—160° F in a volume of liquor of 1 : 20, the bath containing 40—80 lbs. Mordant for Acetate Silk per 100 gallons. Subsequently the material is hydroextracted and dyed with

out rinsing. In addition to the dyestuff, 1—2% acetic acid is added to the cold dyebath, the temperature of which is gradually raised to 160° F. After dyeing the silk is thoroughly rinsed and, if desired, scrooped.

Nevertheless, the use of basic dyestuffs is practically limited to pure acetate silk for the production of very bright shades. Both these processes are unsuitable for dyeing mixed fabrics.

Cellit Fast dyestuffs. The Cellit Fast dyestuffs dissolve readily in hot water to a clear solution without any addition. They are dyed similar to direct cotton dyestuffs without soda, for $\frac{3}{4}$ —1 hour at 160—170° F. According to the depth of shade 20—50% calcined Glauber's salt or chloride of ammonia are added, the proportion of goods to liquor being 1 : 30. Acetic acid may also be added to the bath. When dyeing Cellit Fast Yellow GGN it is absolutely necessary (in order to utilise the dyestuff completely) to add 3—5% acetic acid 30%, in addition to 20—30% Glauber's salt. After dyeing the goods are well rinsed and scrooped as usual. Apart from this very simple method of working, the Cellit Fast dyestuffs are remarkable for good fastness to washing, very good levelling and from good to very good fastness to light. The Cellit Fast dyestuffs as a rule are employed for dyeing pure acetate silk fabrics and hanks. Cotton and kindred fibres generally are not very strongly tinted and it is possible to produce on mixed fabrics of these fibres and acetate silk solid or two-colour effects in one bath on stockings, knitted goods or linings. Wool and silk are strongly dyed by Cellit Fast dyestuffs which, therefore, cannot be used for mixed goods containing these fibres.

The Celliton and Celliton Fast dyestuffs, on the other hand, are insoluble in water and are supplied to the trade in the form of fine pastes. Dyeing is best carried out for $\frac{3}{4}$ —1 hour at 160—170° F in soft water containing 2—3 lbs. Marseilles soap per 100 gallons, the dyestuff paste, which previously has been well stirred and mixed with soft water, being added through a fine sieve. After dyeing the goods are rinsed and, if necessary, scrooped. The feature of these dyestuffs is: good levelling, good fastness to washing and water, from good to very good (and in the case of the Celliton Fast colours excellent) fastness to light. As they are also highly suitable for dyeing mixed fabrics of *animal* fibres and acetate silk (in addition to their use for pure acetate silk fabrics or hanks) these dyestuffs

deserve special attention, the more so as they may also be employed, like the Cellit Fast dyestuffs, for dyeing mixed fabrics of acetate silk and cotton or the older qualities of artificial silk.

If the goods are required to satisfy the highest demands in fastness to washing and water, or if effects are to be produced which, in addition to being fast to cross-dyeing, must to some extent withstand acid boiling, the *Cellitazols* must be used. These dyestuffs, to give fast shades, are diazotised and developed on the fibre.

The *Cellitazols* are dissolved and dyed according to the method mentioned in the respective I. G. pattern-cards.

The dyestuffs discussed in the foregoing are typical acetate silk colours. Their affinity for animal and vegetable fibres, on the other hand, is small. Only the Cellit Fast dyestuffs possess a great affinity for wool and silk. With the above acetate silk dyestuffs and suitable cotton, wool or silk colours it is therefore possible to produce, on mixed fabrics of every description, multicoloured effects or solid shades in one or several baths, according to the kind of material in question.

Acetate Silk mixed with cotton or artificial silk. Such mixtures are used for stockings (e. g. acetate silk stockings with cotton heels, toes and tops) knitted goods of every description, linings and hangings. If the acetate silk is required to remain white, dyestuffs are used which do not stain acetate silk. A large number of them is available.

When using *direct cotton dyestuffs* the dyebath is prepared with the necessary dyestuffs and dyeing carried out, according to the depth of shade, for $\frac{1}{2}$ —1 hour at 120—170° F. with addition of 5—20% Glauber's salt. Additions of alkalis, such as soda, must be avoided.

Diazotising dyestuffs are dyed as mentioned above. After dyeing the goods are rinsed, diazotised cold as usual and treated with a suitable developer. Beta naphthol developed dyeings, to obtain a clear white on acetate silk, after developing must be soaped warm. If the dyeings must be very fast, *Indanthren dyestuffs* may be used. For this purpose the required quantity of such Indanthren dyestuffs (which may also be dissolved according to the IW or IK process) are reduced in the usual way with caustic soda and Hydrosulphite. 5—20 lbs. Glauber's salt fused and 5—10 lbs. Resist for Acetate Silk (to prevent the staining of the acetate silk) are then add-

cd per 100 gallons dyeliquor according to the depth of shade required and dyeing carried out *cold* for about $\frac{1}{2}$ —1 hour. The material is then rinsed, aired, rinsed again and soaped at about 160° F with 2—3 lbs. Marsilles soap per 100 gallons. Care must be taken that not more than $\frac{2}{5}$ pint caustic soda 72—76° Tw. are contained in 100 gallons dyeliquor.

If, on the other hand, the cotton or artificial silk is to be left white, the acetate silk is dyed with suitable Celliton or Celliton Fast dyestuffs or Cellitazols, best in a light soap lather at about 160° F. The cotton or artificial silk, according to this method, will be slightly tinted after dyeing. If desired, it may be cleared by the following method: The goods are either treated for a short time at about 120° F with $1\frac{1}{2}$ pints sulphuric acid 168° F per 100 gallons and rinsed well, or for $\frac{1}{4}$ hour at 100° F in a bath containing about 3 lbs. Blankit I per 100 gallons, keeping them in motion, and finally rinsed.

For the production of solid shades and two-colour effects the acetate silk dyestuffs referred to and also direct, diazotising and Indanthren dyestuffs which do not, or only slightly, stain the acetate silk may be used.

Direct dyestuffs are preferably dyed in one operation, either in the soap-Glauber's salt bath along with Celliton and Celliton Fast dyestuffs (dyeing temperature 140—160° F) or in a Glauber's salt bath with Cellit Fast dyestuffs at the same temperature. After dyeing the material is rinsed and finished. The Cellitazols are used less frequently, as the process requires the use of two baths. They are, as a rule, employed only for the production of solid blacks.

If diazotising dyestuffs have been used for the cotton, the acetate silk is dyed in a fresh bath, at 120—170° F, with Celliton or Celliton Fast dyestuffs with addition of 2—3 lbs. soap per 100 gallons, or with Cellit Fast dyestuffs in the Glauber's salt bath at 120—170° F. The clearness of the effects is increased by a thorough rinsing.

The cotton being dyed with Indanthren dyestuffs, the acetate silk is advantageously dyed in the soap bath with Celliton or Celliton Fast dyestuffs, or with Cellit Fast dyestuffs in a fresh bath with the addition of Glauber's salt.

Mixed fabrics of wool and acetate silk. If the wool only is to be dyed, neutral dyeing wool colours which exhaust from a Glauber's salt bath at 160—175° F and dye the wool

only, may be used. Acid colours may also be employed which, when dyed with 3—5% formic acid and 10—20% Glauber's salt, give sufficiently dark shades at a dyeing temperature of not more than 175° F. This dyeing temperature must not be exceeded, particularly if clear effects are desired. Boiling must be avoided under all circumstances. Two-colour effects or solid shades are dyed either by using the Celliton and Celliton Fast dyestuffs in conjunction with suitable neutral dyeing wool colours, at about 160—175° F, or by first dyeing the acetate silk in the soap bath, rinsing and then covering the wool with weakly acid dyeing brands which affect acetate silk only slightly or not at all.

Fabrics of silk and acetate silk which are already being produced to a large extent, may be dyed both in one and in two baths. The one-bath method is preferably used for solid shades, suitable direct or acid dyestuffs being combined with Celliton and Celliton Fast dyestuffs. When acid dyestuffs are used, the dyebath is prepared with 10—15% Glauber's salt cryst. and 4—8% acetic acid 30% or 1—2% formic acid 85% and the necessary quantities of dyestuff. If the dyeing is to be done with direct dyestuffs they are applied either in a neutral bath or in one acidulated with about 1—2% acetic acid 30%.

If very clear effects are required the two-bath process is preferable to the one-bath process. The real silk in this case is filled up in a fresh bath, using dyestuffs which leave the acetate silk unstained.

Unions and half-silk fabrics, i. e. materials consisting of wool or silk with artificial silk and acetate silk, are dyed as described above. Very striking three-colour effects can be produced on mixed fabrics composed of *real silk, acetate silk and viscose*. In the case of such goods the viscose and acetate silk is at first dyed at about 85° F. Subsequently the silk is filled up with suitable dyestuffs in a fresh, slightly acid bath at about 140° F.

Particularly clear three-colour effects are best produced in three baths, acetate silk, viscose silk and silk being covered consecutively. If it is desired to have the real silk effects very clear, the use of Katanol W is recommended; this product prevents the direct dyestuffs being taken up by the silk.

Mixed fabrics which, in addition to acetate silk, contain wool and artificial silk or cotton are dyed similarly.

As regards the dyeing of fancy tissues consisting of *wool, real silk, acetate silk and vis-*

cose, the wool and silk are dyed first, the viscose and the acetate silk are then covered in a fresh bath with direct and Celliton or Celliton Fast dyestuffs. If it is desired to obtain particularly clear effects, the acetate silk is covered first and then the viscose with addition of Katanol W.

The processes discussed show the many possibilities open to acetate silk in the textile industry.

When dealing with this kind of artificial silk a certain amount of care must always be exercised. It is greatly affected by heat and also too hot water and steam, so that it is necessary to use great care when ironing or pleating acetate silk as otherwise its feel and lustre is impaired. Too hot drying on the

drying cylinder, hot calendering or strong decatizing should as far as possible be avoided. Acetate silk has only poor absorbent properties and aqueous solutions, consequently, penetrate into it only with difficulty. The usual sizing and finishing agents therefore cannot be used in connection with it. Sizes and finishes made up with glue or tragacanth as a base have proved to be most suitable in this respect.

The silk-like appearance, the agreeable feel and a very great fineness of thread are properties of acetate silk which, in addition to its peculiar behaviour in mixed fabrics, have given to this latest kind of artificial silk an importance in the textile industry which bids fair to be permanent.

The Printing of Acetate Silk and Fabrics containing Acetate Silk

By *Gmelin and Kerth*

In recent years the dyeing of acetate silk has made considerable progress, and the printing of this artificial fibre has also met with an ever increasing interest. Owing to the peculiar behaviour of acetate silk, which differs from that of the other textile fibres, and which facilitates the production of pleasing colour combinations and striking effects, this fibre is being used for a large variety of printed styles. As the experience gathered during the last few years has enabled one to adapt the dyeing or printing method of the existing ranges of dyestuff to the peculiar properties of the acetate silk, and as entirely new groups of dyestuffs, which, when dyed or printed by special methods, possess an affinity for this fibre exclusively, it seems advisable to give a brief survey of up-to-date printing methods, both as regards fabrics of acetate silk only, as well as of mixed fabrics containing acetate silk.

A. The printing of all-acetate silk fabrics

The following particulars regarding the various printing methods refer to material which has been desized and prepared for printing.

It should be noted that during the wet treatment of fabrics containing acetate silk, both in dyeing and printing, temperatures of more than 175° F., and liquors containing fixed alkalis are to be avoided; otherwise the lustre of the acetate silk would be impaired, and saponification would be set up.

The methods used for printing calico with

basic acid, mordant, and vat dyestuffs, and with the Indigosols and Diphenyl Black, may, with slight modifications, be applied to acetate silk up to a certain point. The thickening used for acetate silk is usually composed of gum and British gum.

Basic dyestuffs are fixed on acetate silk with the aid of a tannin mordant, or by adding about 20 parts Celloxane or Mordant for acetate silk to 1000 parts of the print paste, followed by steaming, or, in the case of the tannin mordant, by a treatment with antimony salts.

The printing method with the aid of tannin mordant is particularly suitable for black styles produced with Printing Black VX.

Acid-dyeing wool dyestuffs. Of this class, only a few are suitable for the direct printing of acetate silk. These dyestuffs are dissolved with the aid of Glycine A or Fibril D, oxalate of ammonia is added to the print paste, and after printing, the goods are fixed by steaming for ½ hour without pressure. Steaming is followed by rinsing in cold water.

Examples of such acid dyestuffs are:

Victoria Yellow O,
Indian Yellow G, R,
Orange II, IV, RO,
Brilliant Orange ON,
Sorbine Red G,
Fixing Scarlet G, R,
Scarlet for Silk G,
Fast Red O, 3GX, AV,
Victoria Fast Violet B extra.

Most of the *mordant colors* are only suitable for fabrics of cotton + acetate silk. But some of the chrome colors, e. g.

Alizarine Yellow GG in paste,
Gallo Violet DF, DFM 27964,
Gallo Heliotrope BD,
Chrome Turquoise Blue B,
Chrome Green GD extra,
Gallo Indigo Blue S, SR, BGG,
Celestine Blue B,
Gallo Fast Green SK,
Gallo Blue E,
Gallo Grey GP,
Gallo Fast Grey B,
Gallo Navy Blue GGD, S,

may be printed on all-acetate silk fabrics in the manner usual for cotton fabrics.

All these mordant colors, with the exception of Alizarine Yellow GG and Gallo Fast Green SK, give fast to soaping prints on all-acetate silk fabrics even without chrome mordant. As this method produces purer effects and leaves the goods in a softer condition, it is preferred to the one for which a chrome mordant is used.

Chrome Turquoise Blue B and Chrome Green GD extra may, in place of acetate of chrome, be printed with the addition of 2% Celloxane, and give bright but not very full prints. They are printed with a gum — British gum thickening, preferably with the addition of a solvent such as Glycine A and Butanol.

Those of the *Vat dyestuffs* which may be printed by the potash or soda-Rongalite steaming process, may be used for the printing of acetate silk and acetate silk mixtures. The partial saponification of the cellulose ester is, according to the experience gained hitherto, without deleterious influence on the lustre of the acetate silk. After steaming in the Mather Platt or in the Indanthren rapid steamer, it is advisable to pass the goods at full width through a bath at 120—140° F., containing 1 part bichromate and 5 parts acetic acid 30% per 1000; this is followed by rinsing and soaping at 160—175° F.

The *Indigosols* are used for the production of prints or padded styles on acetate silk by the nitrite or bichromate process. However, satisfactory and fast to soaping prints are only obtainable provided the goods, before developing, are steamed for 5—20 minutes and provided developing is carried out at a higher temperature and for a longer period than is usual with cotton.

The solution of the Indigosol dyestuff, suit-

ably thickened with tragacanth, is printed or padded with the addition of 25—30 parts sodium nitrite and some ammonia to the print paste, the goods are then dried, steamed for a correspondingly long period and developed at 165—175° F. for 2—4 minutes in a bath containing 30 parts sulphuric acid 168° Tw. per 1000 parts liquor, together with some urca, after which they are washed and soaped at 140° F. (Patent for this process has been filed by Messrs. Durand & Huguenin S.A.).

Fine black prints may be produced on acetate silk with *Diphenyl Black Base I* by the same printing method as usual for cotton.

Of special importance for the printing of acetate silk are the special dyestuffs for this fibre, viz. the *Cellit Fast*, the *Celliton*, and the *Celliton Fast dyestuffs*.

The Cellit Fast dyestuffs are printed with the addition of 20—50 parts of a solvent such as Glycine A, aceto acetic ester or Butanol per 1000 parts print paste. The addition of calcium thiocyanate and Resorcine in the proportion of 40—50 parts per 1000 parts print paste will produce deeper prints.

The Cellit Fast dyestuffs suitable for direct printing are:

Cellit Fast Yellow GGN, R (the latter is somewhat phototrope and therefore unsuitable for mixtures),

Cellit Fast Orange G,

Cellit Fast Red B, BB,

Cellit Fast Rubine B,

Cellit Fast Violet 4R, ER,

Cellit Fast Blue A (this brand gives good results even without acetoacetic ester and calcium thiocyanate).

The Celliton and Celliton Fast dyestuffs which are particularly suitable for printing, are the following:

Celliton Fast Yellow G in paste,

Celliton Printing Yellow 3R in paste,

Celliton Red R in paste,

Celliton Fast Pink F3B in paste,

Celliton Fast Red Violet R in paste,

Celliton Fast Violet B in paste,

Celliton Blue extra in paste,

Celliton Fast Blue B in paste, BB in paste.

These dyestuffs are best printed in fine dispersion in the presence of a suitable emulsifier such as Glycine A.

After the goods have been printed with the dyestuffs referred to, they are steamed without pressure for ¼—½ hour, rinsed and, if necessary, soaped at 140° F. Some of the Celliton and Celliton Fast dyestuffs may be satis-

factorily fixed simply by a short steaming in the rapid ager.

These two groups of acetate silk dyestuffs give very bright shades, the Cellit Fast and Celliton Fast dyestuffs being also very fast to light.

For the *discharge printing* of acetate silk fabrics it is necessary to replace the Rongalite C generally used in cotton discharge printing by *Decroline soluble conc.* or *Hyraldite Z soluble conc.*, which is printed, thickened with gum, according to the depth of the desired shade, in the concentration of 150—250 parts per 1000 parts print paste. An addition of Anthraquinone and acetine in some cases improves the discharge effect. For colour discharges the basic dyestuffs, which are fast to Hydrosulphite, viz.

Rhodamine,
Auramine,
New Methylene Blue etc. but also
Gallo Navy Blue GGD and
Gallo Violet DF, DFM 27964,

may be added to the above mentioned white discharge. After printing, the goods are steamed for 5 minutes in the air-free rapid ager, then washed.

Dyeings produced with basic dyestuffs with the aid of Mordant for acetate silk or Celloxane are, with the exception of Brilliant Rhoduline Violet R, Turquoise Blue BB and Rhoduline Blue 5B hardly to be recommended for discharge grounds, as apart from the exceptions referred to, they are on exposure subsequently tinted in the discharged places. On the other hand the following acid dyestuffs:

Indian Yellow G, R,
Brilliant Orange ON,
Orange IV,
Silk Red G,
Scarlet for Silk N, G,
Fast Red AV, O and
Victoria Fast Violet B extra

may be discharged to a white with the above mentioned white discharge.

The *Cellit Fast dyestuffs* dischargeable to a white are the following:

in full shades
Cellit Fast Yellow GGN, R
Cellit Fast Red BB,
Cellit Fast Violet 4R.

in pale shades
Cellit Fast Rubine B,
Cellit Blue R.

The following brands are suitable as ground for pale colour discharges:

Cellit Fast Orange G,
Cellit Brown G,
Cellit Fast Red B,
Cellit Violet RR.

Among the *Celliton* and *Celliton Fast dyestuffs*, the following are also dischargeable to a white:

Celliton Fast Yellow paste and
Celliton Red R paste.

B. The printing of mixed fabrics containing acetate silk

1. Mixtures of cotton and Acetate Silk.

With mixed fabrics of acetate silk and real silk or some other artificial fibre, the peculiar dyeing behaviour of the acetate silk is a special feature, which may also in the production of prints be used for the creation of beautiful and novel colour effects of great variety.

As the behaviour of viscose silk is on the whole like that of cotton, the particulars given for cotton and acetate silk fibres also apply to viscose + acetate silk fabrics. After the goods have been desized with Biolase N extra powder, they are, if necessary, bleached by placing in a chloride of lime solution of 0.37° Tw., soured off with acetic acid or formic acid, then treated for 2 hours in a hydrogen peroxide bath.

In the production of direct prints on mixed fabrics of cotton or viscose silk + acetate silk, either one or the other fibre may be left undyed, or both fibres may be dyed the same shade or in different shades, by selecting suitable dyestuffs or dyestuff combinations. To this end, the goods are printed with suitable *direct dyestuffs* along with *Cellit Fast*, *Celliton* or *Celliton Fast dyestuffs*, and fixed by steaming. The direct dyestuff will be fixed on the cotton whereas the other dyestuff will be fixed on the Acetate silk only. In order to ensure pure shades, it is, however, advisable when such combinations are produced, to make a careful selection among the dyestuffs which come into question. Moreover, after steaming, the goods must be washed very carefully and, if necessary, given a light soaping for the removal of dyestuff which has not been fixed and which only adheres loosely.

Examples for print pastes:

Print Paste I

10— 40	parts	of a direct dyestuff,
10— 20	„	of a Cellit Fast dyestuff,
30	„	Glycine A,
30	„	Butanol,
390—350	„	water,
200	„	British gum powder,
300	„	gum Senegal (1 : 1),
30	„	sodium phosphate
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1000	parts	(by weight).

Print Paste II

10— 40	parts	of a direct dyestuff,
25— 50	„	of a Celliton or Celliton
		Fast dyestuff in paste,
30	„	Glycine A,
405—350	„	water,
200	„	British gum,
300	„	gum Senegal (1 : 1),
30	„	sodium phosphate
<hr/>		
1000	parts	(by weight).

After printing, the goods are steamed for 1 hour, then washed thoroughly, first cold, then lukewarm, if desired soaped at 85° F. with ½ part Marseille soap per 1000 parts liquor, rinsed and dried.

The following *Cellit Fast*, *Celliton* or *Celliton Fast* dyestuffs leave cotton or viscose silk unstained or practically unstained in printing:

Cellit Fast Yellow GGN, R,
Cellit Fast Orange G,
Cellit Fast Red B,
Cellit Fast Rubine B (tints slightly),
Cellit Fast Blue A,
Celliton Fast Yellow G paste,
Celliton Printing Yellow 3R paste (tints slightly),
Celliton Red R paste (tints slightly),
Celliton Fast Pink F3B paste,
Celliton Fast Red Violet R paste,
Celliton Fast Violet B paste,
Celliton Fast Blue B paste, BB paste.

The number of direct dyestuffs which leave acetate silk unstained or practically unstained in printing and which dye the cotton or viscose silk, is a very large one. The following list contains a selection of these, those which are dischargeable with Rongalite being marked with an *):

Yellow:

Sirius Yellow *R extra, 5G,
Dianil Yellow *RR, GC,
Chrysofenine G.

Orange:

Sirius Orange G,
*Benzo Fast Orange WS,
*Dianil Fast Orange O,
Pyramine Brilliant Orange 3RS.

Red:

*Sirius Red 4B,
*Sirius Rubine B,
Sirius Pink BB, *G,
*Sirius Red Violet R, B,
Sirius Scarlet B,
*Diamine Fast Scarlet 8BSE,
*Diamine Fast Rose G, B,
*Dianil Light Red 12BW.

Violet:

Sirius Violet *3B, BL,
*Diamine Fast Red Violet FR,
*Benzo Violet RL extra,
*Dianil Violet AR.

Blue:

*Sirius Blue 6G, G, BRR, BR, B,
*Benzo Fast Blue GGL, R,
*Benzo Fast Blue FFG,
*Chicago Blue 6B,
*Diamine Blue 3B,
*Benzo New Blue 5B,
*Diamine Black BH.

Green:

Dianil Green AG.

Brown:

Sirius Brown R,
Dianil Brown AR,
*Pegu Brown G.

Grey and Black:

*Sirius Grey G, R,
Dianil Black A2B,
*Cotton Black A4G,
*Diazanil Black AV.

In place of the direct dyeing dyestuffs, several of the Chrome dyestuffs, e. g.

Alizarine Yellow CY,
Chrome Yellow DF extra,
Azol Printing Orange R,
Chrome Fast Orange RD,
Azol Printing Red BB extra,
Chrome Fast Red BD,
Chrome Red Brown 5RD,
Azol Printing Violet RR extra,
Chrome Brilliant Violet BD,
Alizarine Viridine FF,
Naphthomelane SB,

may be printed on fabrics of cotton + acetate silk in combination with Cellit or

*) The „Sirius“ colours are sold in the USA and Canada under the designation „Fastusol“.

Celliton dyestuffs, the mordant dyestuffs being fixed on the cotton and staining the acetate silk but slightly.

The peculiar behaviour of the Indigosols in relation to acetate silk permits the use of these dyestuffs, so highly valued on account of their fastness, for the production of the most varied effects on fabrics of cotton or viscose silk + acetate silk. For instance, if the goods are printed or padded with an Indigosol dyestuff, according to the nitrite process described above for all-acetate silk fabrics, both fibres are dyed approximately the same shade. On the other hand, if the fabric, printed or padded by the nitrite process, without previous steaming, is developed for 15—30 seconds at 75—85° F. in a sulphuric acid bath, then well washed and soaped at 140—160° F., only the cotton or viscose silk is dyed, the acetate silk remaining white. If it is desired to stain the acetate silk only and to leave the cotton or viscose silk white, the fabric is printed or padded with the Indigosol without the addition of nitrite to the print or padding paste, steamed for about 15 minutes after drying, well washed and soaped and subsequently developed for 1—2 minutes at 160—165° F. in a bichrome bath containing 5 parts bichrome and 20 parts sulphuric acid at 168° Tw. per 1000 parts liquor.

Developing may in place of the chrome bath be carried out for ½ minute at 120° F. in the nitrite bath containing 10 parts sodium nitrite and 5 parts sulphuric acid per 1000. The soaping preceding developing will remove the Indigosol from the cotton or viscose silk but not from the acetate silk. If the second and third processes are combined, both kinds of fibres may, of course, be dyed in different shades, and by padding twice with suitable Indigosols, fine shot effects may be obtained on fabrics of cotton or viscose silk + acetate silk. (Patent for this process has been filed by Messrs. Durand & Huguenin S. A.)

Indigosol Green IB, owing to its pronounced affinity for the cellulose fibre cannot be used for this purpose as it is not removed sufficiently from the cotton or viscose fibre by soaping.

In *discharge printing*, the discharge recipe recommended for discharge prints on all-acetate silk fabrics, for which Decroline soluble conc. or Hyraldite soluble coc. is used, is also employed in order to ensure uniform discharges on mixed fabrics dyed in solid

shades with dischargeable direct dyeing and Cellit or Celliton dyestuffs. Particulars of the dischargeable Cellit and Celliton dyestuffs will be found on page 113. Colour discharges are produced by adding discharge-resisting basic dyestuffs to the discharge paste, the basic dyestuffs being advantageously fixed by means of the usual preparation, viz. Katanol O or W, instead of adding tannic acid to the print paste; this preparation may either be carried out simultaneously with the dyeing process or by subsequent immersion in a Katanol solution.

On dyeings of mixed fabrics with dyestuffs which are partly dischargeable and partly discharge-resisting, multicoloured discharge effects are obtained on both fibres by printing with the Decroline discharge.

In the case of solid shades for which discharge-resisting dyestuffs were employed to dye the acetate silk, e. g.

Celliton Fast Pink F3B,
Celliton Fast Violet B,
Celliton Blue extra,
Celliton Fast Blue B and BB,

only the cotton will be discharged when printed with an ordinary Rongalite C discharge, whereas the acetate silk remains coloured.

2. *Mixed fabrics of wool + acetate silk.*

The desized goods are bleached with hydrogen peroxide as usual with wool-goods to be printed, given an acid chemicking, care being taken to avoid too severe chemicking.

For two-colour effects in direct printing, those of the acid dyeing wool dyestuffs are used which leave the silk particularly clean, either alone or in combination with Celliton or Celliton Fast dyestuffs, according to whether the acetate silk is desired as white or as colour effect.

The Celliton dyestuffs suitable for the printing of mixed fabrics of wool + acetate silk, although they stain the wool more or less but still within the permissible limits, are the following:

Celliton Fast Yellow RR paste,
Celliton Fast Pink F3B paste,
Celliton Red R paste,
Celliton Fast Violet B paste,
Celliton Fast Blue B paste.

The combination of the acid wool dyestuff and the Celliton or Celliton Fast dyestuff is printed, adding Glycine A and oxalate of ammonia to the print paste. The goods are

steamed for 1 hour, thoroughly washed, first cold, then lukewarm, then soaped, as may be necessary.

The following is a selection of acid dyeing wool colours, which, in printing, leave the acetate silk white:

Yellow:

Flavazine S,
Supramine Yellow R,
Tartrazine O.

Orange:

Fast Light Orange G,
Orange GG.

Red:

Acid Anthracene Red 5BL,
Brilliant Scarlet 6R,
Supramine Red GG,
Palatine Scarlet 3R,
Amido Naphthol Red BB.

Violet:

Acid Violet 4RN,
Alizarine Direct Violet EBB.

Blue:

Cyanine B,
Alizarine Direct Cyanine 3GE,
Sulphon Cyanine brands,
Azo Wool Blue SE.

Green:

Alizarine Direct Green 5G,
Alizarine Cyanine Green G extra,
Wool Green S,
Light Green SF yellowish.

Brown:

Sulphon Acid Brown RR, 4R.

Grey:

Acid Alizarine Grey G,
Palatine Black MM.

Discharge prints on mixed fabrics of wool and acetate silk can be produced in a man-

ner similar to that usual with other mixed fabrics, along with Decroline sol. conc., but they are of minor interest.

3. Mixed fabrics of real silk + acetate silk or real silk + viscose + acetate silk.

Such fabrics are cleansed, before printing, by being taken through a warm soap bath (120° F) containing 3 parts Marseille soap and 1—2 parts ammonia per 1000 parts liquor.

The printing methods are very similar to those described for wool and acetate silk. For two-colour effects, combinations of suitable Celliton or Celliton Fast colours with such acid or direct dyestuffs as leave the acetate silk practically unstained, are used. Should a three-colour effect be desired in the presence of viscose silk, a selection is made from those direct dyeing dyestuffs which, in addition to the acetate silk, also leave the real silk unstained as far as possible, and from those acid dyeing dyestuffs which stain both the acetate silk and the viscose silk as little as possible, besides of course the Celliton dyestuffs.

Of the Celliton Fast colours, Celliton Fast Yellow G, Celliton Printing Yellow 3R, Celliton Red R, Celliton Blue extra, and Celliton Fast Blue BB stain real silk fairly strongly, Celliton Fast Yellow RR, Celliton Fast Pink F3B, Celliton Fast Red Violet R, Celliton Fast Violet B, and Celliton Fast Blue B only slightly.

The dyestuff combination consisting of acid or direct dyeing dyestuffs and Celliton or Celliton Fast dyestuffs is printed along with Glycine A, some ammonia and alum or, in the presence of direct dyeing dyestuffs along with sodium phosphate, steamed for 1 hour with moist steam, then washed thoroughly, first cold, and then lukewarm.

The Acme of Achievement in the Production of Auxiliary Media for the Textile Industry

By Dr. W. Kling

The field of activity represented by auxiliary products is the subject of much controversy nowadays. Opinions differ widely, both for and against. Yet the actual expansion which has taken place in the manufacture of such products—the rise of this branch industry from its modest beginnings to the commanding position it occupies to-day—testifies more eloquently than any amount of

theorizing to the existence of a real demand for good auxiliary products. To ascribe this rapid development to the effect of mere advertising would be most unfair to our textile industry, in the face of its manifold achievements in every one of its branches. Clear proof of the relative importance of aids to textile finishing is furnished by the fact that our largest national chemical enterprise, the

I. G. Farbenindustrie A. G. of Frankfurt, has taken steps just lately to devote special study to this branch of activity.

The divergence of opinions as to the value of the various textile auxiliary products may be explained by stating that clear knowledge is as yet lacking both as to the properties which a good auxiliary product should possess and as to the application of any simple method of testing it for the possession of such properties. We propose presently to try and describe an ideal auxiliary product. Next to this we will endeavour to show, by reference to the manufactures of the firm of H. Th. *Böhme* A. G. Chemnitz, how much progress has been made towards the attainment of that ideal.

When we refer to textile finishing we intend that term to comprise all the intermediate chemical processes which transform textile fibres from the raw state into the finished commercial product. These processes include washing, bleaching, dyeing and chemical finishing, as well as certain special processes such as carbonizing and mercerizing, which, as we know, are of considerable importance to-day. The wideness of the range covered by these manifold processes will at once make it clear that our ideal product will have to meet very exacting demands, not always in harmony, indeed occasionally in actual conflict with each other. None the less I propose to tabulate a few of the properties most generally called for, and in doing so I want to make a distinction between qualities which I will call indispensable and others which are of especial value.

The indispensable requisites are those which the product must possess so that it shall not itself be actively responsible for bad qualities in the finished article, as it would be for example if it caused the formation of precipitates, if it attacked the textile fibres etc.

Qualities which will yield definite advantages over and beyond the results customarily aimed at in the finishing process we must class as valuable, because it is these which constitute the real usefulness of any auxiliary product.

Perhaps we may therefore differentiate as follows:

a) *Indispensable Requisites:*

1. *The product must be as far as possible "neutral" i. e. colourless, free from odour, and nonpoisonous, and must not have the slightest corrosive action upon materials or machinery etc.*

2. *The product must be readily soluble in water.* Water is the most widely used medium, indeed the only one in which any work on a commercial scale is ever done. In order that the product shall retain its full efficiency when added to boiling liquor, it should have a boiling point well above the boiling point of water.

3. *The product must be capable of remaining unaffected* not only by those agencies which cause hardness in water but also by the usual acids and alkalis, oxidising and reducing substances, as well as high temperatures.

b) *Valuable Qualities.*

1. *The power of soaking the fibres* and enhancing the penetrating and permeating powers of the liquor — these latter points being not absolutely synonymous with mere soaking power.

2. *The power of dissolving dyestuffs* and further of finely dispersing such dyes as are commonly met with in the form of coarse-grained highly molecular particles mixed with colloid substances, so that these dye particles are able to find their way into the inner substance of the fibre.

3. *Solvent action upon fatty substances* of all kinds, added to the power of emulsifying such impurities as are insoluble — in other words, *cleansing power.*

4. *Protective and softening action upon the fibres.*

If we finally emphasize that the product must possess all these qualities even when present in very dilute form, so as to be inexpensive in use, we shall probably have enumerated fairly well all the requirements which need to be taken into account.

I should like to add that in my view it is a mistake to speak of "equalising" or "distributing" power, terms which defy any close definition or any practical test. I consider this power — such as it is — to be the sum total and the final outcome of the valuable qualities already referred to.

To summarize briefly, we may perhaps say that an ideal auxiliary product must be capable of remaining unaffected by any compound or by any external conditions with which it may be brought into contact in daily practice. It must possess a high degree of soaking and penetrating power, it must have a pronounced solvent action upon dyestuffs as well as great cleansing power and at the same time it must

protect the fibres, so that the natural softness and flexibility of the material are fully preserved.

If we now examine the auxiliary products which are actually available for the purposes of the textile industry at the present day, we shall quickly recognize that whilst we already have a large number of good and in some respects excellent special products to draw upon, we are still a very long way from the all-round ideal product, which may possibly be altogether unattainable.

For a long time, soap and Turkey red oil held the field unchallenged as the sole representatives of their species. Soap—discovered, according to Pliny, by the Gauls—was long used for none other than cosmetic purposes. Its use on a large scale since the close of the XVIIIth century has been directly due to the growth of cotton dyeing and bleaching. Turkey red oil is of more recent date. Sulphurated oil—viz. olive oil—was first used about the middle of the XIXth century, until the time when the derivate of castor oil, employed in the process to which that oil gave its name, rapidly took its place as a product of importance. If we examine the one and the other in the light of the requirements laid down for an ideal product, they will not carry us very far. Neither will stand the test for No. 2 of the indispensable requisites above set out. Neither of them is capable of withstanding the action of lime or magnesia; soap possesses no power of resistance to acids, and ordinary Turkey red oil very little. There cannot therefore be any thought of employing these two substances for universal requirements without reservation.

Even the notable progress achieved in such directions as the production of the first lime-resisting oil, or the discovery of the pronounced steeping qualities inherent in certain alkalis aromatic sulpho-acids, did no more than meet certain special requirements, and failed to bring us any nearer to the wished-for ideal product.

It did seem that the ideal had been attained when Freiburger hit upon the idea of introducing to the textile industry certain selected heterocyclic bases, well-known to-day under the name of "Tetracarnit". This last combines the indispensable requisites almost without exception: it gives a clear solution in water and is almost unaffected by the outside agencies to which reference has been made. It possesses steeping and penetrating power, its action as a dyestuff solvent and disperser is

universally recognized, and it exerts a cleansing action upon the goods. In practice, this substance has earned a high degree of appreciation in the textile industry by reason of the exceptional manner in which it does combine so many desirable qualities. It has, however, been criticised on the ground that its steeping power is inferior to that possessed by steeping agents pure and simple. The manufacturers replied by producing Novocarnit, the steeping power of which has latterly been so greatly enhanced that it has nothing to fear from comparison with other substances; and also by introducing Oleocarnit, a special product for use in cotton dyeing, which has good steeping power and also acts as a dyeing oil. Both of these products possess in other respects the same essential characteristics as Tetracarnit.

But even Oleocarnit, which would appear to fulfil all the requirements which we have said that an ideal auxiliary for all-round use should possess, cannot in fairness be actually described as such. One circumstance which tells against it is its inadequate cleansing action. It is true that Tetracarnit is still used to-day in special cases as a washing medium, but it could not be used as a substitute for soap (for instance), if only for the reason that apart from its insufficient emulsifying power, it would have to be used at so high a concentration that its cost would be prohibitive and the pungent odour resulting would make the working conditions too unpleasant to be tolerable. We must now put aside the thought of our ideal all-round and turn our attention to the special branch consisting of grease solvents and washing media.

The chief solvents of grease used in the textile industry to-day are chlorinated hydrocarbons, amongst which ethylene trichloride ranks high by reason of its particularly intense solvent action upon grease. It, however, shares with all other chlorinated hydrocarbons the drawback of not being soluble in water. It requires first to have emulsifying power imparted to it by the addition of substances similar to soap or, popularly speaking, it has to be made soluble in water. Whilst these ethylene trichlorides work excellently in wool-washing, they cannot be used in cleansing processes which call for boiling liquor on account of the low boiling-point of the grease solvent. To meet this shortcoming, chemistry has supplied us with the higher chlorinated hydrocarbons and the hydrated phenols, which work efficiently at higher

temperatures. Endeavours are made to get over the diminished resisting power resulting from the addition of soap-like substances by substituting oils possessed of the desired resisting power. It may be mentioned that we are able to-day to obtain commercially certain washing and grease-dissolving compounds such as Lanaclarin which are free from grease and which are quite unaffected by lime or acids.

The dyeing oils constitute a separate branch in themselves. They embody, practically speaking, the last of the desirable features which we have tabulated — the power to protect and soften the fibres. Recent endeavour has been in the direction of enhancing their steeping action and their powers of resistance. Avirol KM Extra is an oil which in this respect goes a long way towards satisfying the most exacting demands of the practical worker. Its steeping power is practically equal to that of the best recognized steeping media pure and simple. Even where very hard water is used, there is no separation or precipitation of solid, sticky lime soap. Its resistance to acids is so great that the product can be used in acid wool-dyeing processes with the most satisfactory results. The summit of achievement in regard to magnesia-resisting powers in particular can be claimed on behalf of Avirol E Finish, which gives a clear solution in liquor containing bitter salts even at such high concentration as 1 to 1. The composite

products Floranit M and Eucarnit show a very creditable measure of achievement in regard to acid and alkali-resisting power; the former is acknowledged as a valuable addition to mercerizing liquors, and the latter as a helpful ingredient of carbonizing liquors. For the softening of artificial silk, which constitutes nowadays quite a problem in itself, olive oil derivatives are largely preferred to the castor oil products. In this special field also we have to-day such products as Brillant Avirol SM 100 which yield very good results.

On looking back, the reader will see that in discussing the actual situation as it is to-day we have got further and further away from the ideal product of universal applicability which all of us are still waiting for. We are still a long way from it, indeed this one and only universal article will probably remain for ever unattainable. The chemical industry, however, if we avail ourselves of its best achievements, amongst which the special products mentioned as examples must certainly be included, places at our disposal auxiliaries which when used for the special purposes to which they are adapted, yield highly satisfactory results. Its task for the future will be to concentrate upon making these special products still more perfect, so that their range of application, still rather limited to-day, may be extended as far as possible if not indefinitely, so that eventually the whole character of the subject may be simplified.

Black and navy blue shades, dischargeable to white, on pure acetate silk

By Dr. Fischer

As a result of the growing importance of acetate silk, the printing of fabrics produced from this fibre also is steadily on the increase. At first mixtures of acetate silk and cotton claimed the chief interest, lately, however, there is also a rising demand for pure acetate silk fabrics, in particular voiles.

Generally speaking, the production of print-on styles on acetate silk offers no difficulties. For this purpose the special dyestuffs for acetate silk: Cellit, Cellit Fast and Celliton dyestuffs, also basic dyestuffs in conjunction with Celloxane or Mordant for Acetate Silk and a large number of Indanthren or Algol dyestuffs, are used on account of their simple method of application, the partial saponifica-

tion of the fibre through the alkali contained in the print colour, being put up with.

It is more difficult to produce good discharge prints on acetate silk fabrics. The number of dyestuffs of good dischargeability is limited. Blotches dyed with Cellit Fast Yellow GGN, R, Cellit Fast Yellow G, Celliton Orange GR, Cellit Fast Red B, BB, Celliton Red R, Cellit Fast Rubine B, Cellitazol ORB (Developer: Beta Naphthol), Cellit Fast Violet 4R, Cellit Blue R, Cellitazol B (Developer ON), Cellitazol ORB (Developer: Phenol) are dischargeable. To enlarge the scale of shades it is, however, often necessary to make use of basic dyestuffs, such as Bismarck Brown FR extra, Brilliant Rhoduline