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RECENT DEVELOPMENTS IN DYEING 1/

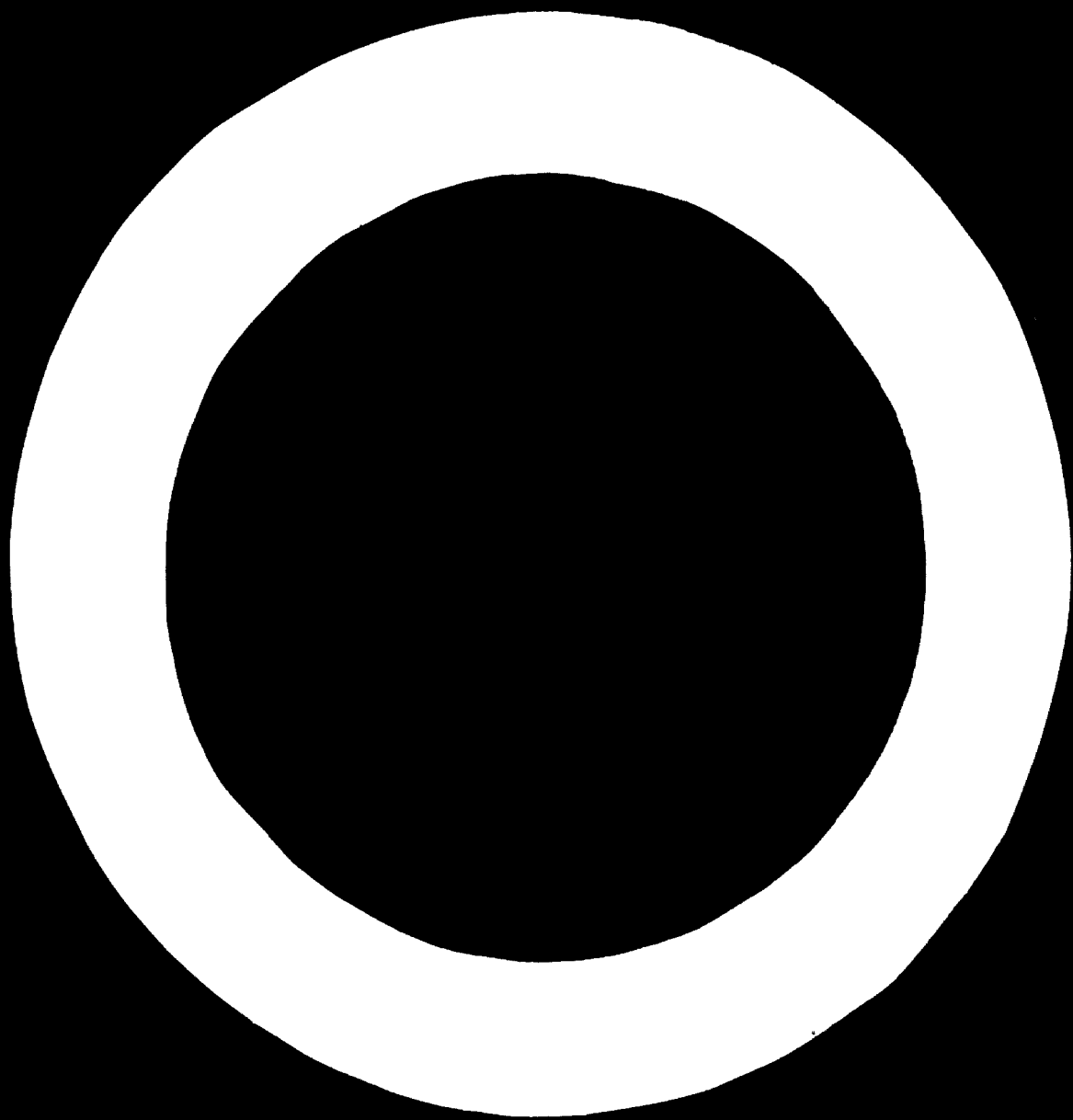
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In the preparatory work carried out before writing this paper, there came to light an article by Newton published under the title "Developments in Dyes and Dyeing 1973/74".¹

This article gives a comprehensive reference list of recent developments and publications but does state in the summary that the period under consideration was a fairly quiet year with regard to new developments on both the dyeing and machinery side. It further states that a number of improvements and refinements had been made on existing methods. It is this theme of improvement and refinement which runs through the following paper, although it is linked as far as possible with the need for simplicity in operation of the methods described.

The emphasis for this paper will be placed on two substrate materials, cotton and mixtures of cotton with polyester fibre as it is these two materials which offer the best chance for an industrially developing country to establish relatively high levels of production in a short time. It is also the type of industry which will produce articles or materials which can be marketed in both home and export areas. The underlying theme of simplicity in operation of the techniques involved in order to achieve the desired result, which is an efficient production plant, is an important factor for industries in developing countries where the labour force has to be trained from first principles.

Now that the substrate around which the operation will be built has been defined, the dyeing of cotton and cotton/polyester mixtures in yarn and piece form will be considered, a logical development from the papers already presented at this Symposium and which fits with the concept of simplicity in processing. Broadly speaking, therefore, the idea is put forward of a manufacturing plant which is producing cotton and cotton/polyester yarn and/or fabric which provides the base material for both a yarn dyeing plant and piece dyeing plant which can feed home or overseas based converters. The major factors which must be considered are as follows:

1. Choice of dyestuff from the technical standpoint.
2. Economic considerations.
3. Dyeing techniques including the machinery necessary.
4. Suitability for industrially developing countries of the proposals made.

1. Choice of Dyestuff

The range of dyestuffs available for the dyeing of cellulose is wide, well-known and well-documented, and because of the long standing use of the material, it is likely that the first fruits of current research work will produce new dyestuffs within existing ranges rather than a complete new class of dye at least within the foreseeable future. The current range of dyes available includes vat and solubilised vat, reactive, sulphur, direct, azoic and pigment. No reference need be made here to any other types available such as mordant or mineral dyes.

The application technology of these dyestuff classes is well understood and will only be referred to in the context of suggested improvements or new developments in machinery or practical application techniques. The major point is to decide which range or ranges of dyestuffs merit most consideration and selection and the reasons for this choice.

Vat Dyestuffs

These offer high fastness properties and a wide range of shades limited only in the bright red and bordeaux areas. Dyestuff costs vary and in general they form the most expensive range in terms of unit price per kilo of dyestuff but this does not necessarily mean they are the most expensive in use.

Reactive Dyestuffs

These dyestuffs also offer high fastness properties but they are in general lower than the vat range but the shade gamut includes some bright colours unobtainable with vat dyestuffs. The methods of application possible include such simple application techniques as the cold-pad-batch method (as do vat dyestuffs) which must be an important point to consider when setting up a new factory where the labour force will be new to the work involved. Both the unit price and the applied price approach those of vat dyestuffs. They are more difficult to wash off after application however, which is necessary to obtain maximum fastness properties and in addition the water requirements are therefore substantially higher than for vat dyestuffs in this respect.

Sulphur Dyestuffs

These dyestuffs must be considered for navy shades, brown shades, black shades because of economic factors but application techniques still require considerable skill and expertise from the operatives and there may be rather more effluent problems than desirable in a developing industry and on the whole the use of sulphur dyes can be considered a less likely choice. Unlike the vat or reactive classes already mentioned, sulphur dyes do not lend themselves to the dyeing of cotton/polyester blends in conjunction with disperse dyes with the possible exception of black shades.

Direct Dyestuffs

This class must be considered as it offers a wide range of available shades, and fastness properties up to a medium level, increased if one includes after-treatments and metallised dyestuffs. The ease of application is also in their favour but in the context of inclusion in a cotton/polyester mixture yarn or fabric direct dyes are open to question from a fastness point of view. In discontinuous dyeing which is mainly for fashion wear, they find considerable use however.

Azoic Dyestuffs

For the production of certain shades, for example, reds or navys on 100% cotton, Azoic dyestuffs cannot be ignored. The application techniques are not chemically difficult but from the practical standpoint a higher degree of care and

expertise is necessary in order to produce satisfactory results. The specialist nature of the shades involved makes it unlikely that azoic dyes would form a significant processing part of our proposed installation, as their application to cotton/polyester blends is also very limited. In addition, physiological hazards, particularly in the production of the azoic dyestuffs themselves, have also decreased very recently the use of this class of dyestuff.

Solubilised Vat Dyestuffs

This is an important range for both cotton and cotton/polyester blends. It is of particular importance for the production of fast to light and washing shades for shirtings and similar fabrics and they can well be incorporated into a cotton/polyester blend fabric from the continuous processing point of view.

Pigment

This class of colour matter is becoming more and more accepted as a means of dyeing pale shades such as are required on shirting fabrics but at the same time incorporating easy care properties by the addition of resin, catalyst and handle modifying products to the pigment/binder system. It is a one-bath one-pass process and as such is attractively simple. The limitation of the system is one of depth of shade, but another of its advantages is the ability to produce pale ground shades which can then be overprinted using a similar pigment system, the dyed ground and overprint then being fixed by one final baking operation.

Having briefly summarised the dyestuff ranges available, the next step is to choose those dyestuffs which are most suited to the postulated production unit in terms of yarn dyeing and continuous piece dyeing.

I 100% Cotton

a) Yarn Dyeing

For reasons of fastness, shade gamut and application possibilities the choice must be:-

Vats (including solubilised Vats)

Reactive

Direct

Azoic

Sulphur

The major proportion will go to vat and reactive dyestuffs.

b) Piece Dyeing

The major dyestuff ranges are:-

Vats (including Solubilised Vata)

Reactive

Pigment

Direct

Azoic

Sulphur

II Cotton/Polyester

In the case of cotton/polyester mixtures the choice of dyestuff for the polyester fibre is of course confined to the disperse dyestuff range. Within that range there is a wide shade gamut and an adequate range of fastness possibilities according to end use requirements.

The dyestuff selection possibilities are therefore as follows:

a) Yarn Dyeing

Disperse/vat
Disperse/reactive
Disperse/soluble vat

b) Piece Dyeing

Disperse/vat
Disperse/reactive
Disperse/soluble vat
Pigment

It was not within the scope of this paper to give a detailed description of the technical application of all dyestuff ranges mentioned, as these are fully covered by the manufacturers' recommendation in the appropriate pattern cards. What is intended is to describe the dyeing process as it applies to our model dyeing plant and point out the recent developments and improvements in methods and machinery which help to simplify the process at the same time giving increased security. First however, we must consider the economics of dye selection.

2. Economic Considerations

This is not simply a matter of unit price per kilo, which in any case varies from country to country according to source of supply, for example, home production or imported dyestuffs. Nor is it a matter of the lowest cost per kilo of dyed material unless one is satisfied with the final end performance. Even then it may prove more economical in the long run to produce fabric at a slightly higher face cost

per kilo by choosing a dye which although initially more expensive has a greater security factor, giving a better guarantee of first-time, first quality production. This will keep re-processing costs to a minimum and result in less disruption of planned working. For best quality production, price should never be allowed to overrule technical judgement and an efficient profitable dyeing unit always achieves the correct balance between the two.

DYEING TECHNIQUES AND MACHINERY REQUIRED

a) Yarn Dyeing

Whether our proposed plant carries out dyeing in package form or on warp beams there can be no doubt that the machinery chosen must be capable of reaching high temperature, that is 130°C. This is essential for the dyeing of cotton/polyester blends in aqueous systems and is also desirable for the high temperature vat dyeing process on 100% cotton yarns which results in shorter dyeing times and more level and penetrated dyeings. Most important of all, the high temperature vat dyeing process for 100% cotton yarns can dispense with the need for a separate bleaching treatment which is an important economic and technical advantage.

The final choice of dyestuff is governed by the end use requirements, and the choice of dyestuff range usually lies between vat and reactive according to shade. For cotton/

polyester blend yarns the usual choice is that of disperse/vat and disperse/reactive. For disperse/reactive dyeing, the two-bath process with or without intermediate reduction clearing is employed where as with the disperse/vat a two-bath process can be used or a one-bath, two-step process. The use of the one-bath, two-step process is made easier by the production by dyestuff manufacturers of balanced mixtures of disperse and vat dyestuffs, e.g. the Cottestren dyestuffs range which is supplied by BASF, where the problem of obtaining the correct balance between the component fibres is solved by pre-mixing the vat and disperse dyes in the correct ratio for 33/67 or 50/50 cotton/polyester blends. In beam dyeing of warp yarns however, one must take care that the beam is not blocked by the high concentration of disperse and vat dye particles, otherwise bursting will occur.

For both package and warp beam dyeing, a sound, well presented package must be presented to the dyeing liquor and it must be thoroughly wetted out to remove entrapped air. The use of an efficient cold-wetting but low foaming agent is useful in this respect and the machine should be filled from the bottom thus forcing entrapped air upwards and out of the machine. In warp dyeing it is beneficial to ensure that the

flanges are drilled with two small diameter holes, say $\frac{1}{2}$ " in diameter, to allow any entrapped air to escape.

Dyeing techniques for reactive dyes in yarn dyeing are those based on exhaustion processes and for vat dyestuffs may be those based on stock vatting, half pigmentation or high temperature techniques. Recent developments in the dyeing field have largely been confined to improvements in operating techniques with the objective of saving time, energy and thereby money. To do this however, means to some extent reducing the safety margins inherent in classical dyeing processes and it is at this point that the value of simplicity of systems comes into its real degree of importance.

In a recent paper published by Schlueter and Weigold ², various methods were discussed for shortened dyeing techniques when dyeing with vat dyestuffs and disperse/vat dye mixtures. It is significant that the introduction to the paper emphasises that the safety margins which may prove expensive, can be reduced without a proportionate increase in the risk of obtaining unsatisfactory results.

Fig.1

After considering the exhaustion and levelling properties of vat dyestuffs in relation to time and temperature, the conclusion is that rapid, and

therefore probably uneven exhaustion, is unavoidable with vat dyestuffs even at low temperature and that levelling must therefore be achieved subsequent to the exhaustion phase. This occupies time and it is very interesting to compare the time taken for equivalent stages of vat dyeing by continuous and discontinuous methods.

Fig. 2

Direct transposition of times is of course impossible but it can be seen that there is ample room for improvement. Some examples, which can be discussed in detail, if desired, are:-

Introduction of dyestuff -

Time saved by adoption of rapid filling and emptying systems assisted by vacuum if necessary, e.g. the Burl-Vac process.

Rinsing -

Can be carried out in half full machines or in a separate machine or system.

Oxidation -

Can be accelerated by steam.

Soaping -

Can be carried out in steam.

Pre-treatment -

Can be combined with the dyeing process by means of special auxiliary products.

The optimum dyeing method for yarn in package form can be obtained by combining these separate steps into a complete process.

Fig. 3

This process optimisation can be extended to the dyeing of cotton/polyester blends in package form by applying the principles outlined to the vat dyeing aspect, and by adjusting the rate of exhaustion of the disperse dyes during the heating up process. This is achieved by grouping together those disperse dyes with similar exhaustion characteristics and by this means reducing the time spent at high temperature which was formerly used to obtain level dyeings. The use of special auxiliary products assists this process which has been extended to include pre-mixed vat and disperse dye ranges such as the Cottestren dyestuffs. Two variations of this process are possible in practice.

Fig. 4

Fig. 5

The practical problem of pre-shrinking cotton/polyester packages has also received attention and by means of special techniques pre-shrinking and dyeing can be achieved in one operation thus reducing costs still further.

Fig. 6

These then are some of the recent innovations developed by means of co-operation between the dye-maker, the dye user and dyeing machinery manufacturers so as to optimise and yet simplify the process of yarn dyeing in package form, both of cotton and cotton/polyester blends.

Obviously the cost element of setting up such apparatus must be considered but in the situation under discussion it is one of new investment and not one of capital expenditure to replace existing machinery still eminently serviceable. Indeed many of the points outlined can be adopted on existing machinery to great advantage. Perhaps the most important item of expenditure would be on the special winding machinery such as that for rockets or Barber-Coleman packages or on adapting existing spindles such as the Schlafhorst types from conical to cylindrical package winding form, where the cost is approximately £11/£12 per spindle, plus the cost of the dyeing former. It is to be expected that the total end cost is cheaper however, due to improvements in the rejection rate, better quality yarn and elimination of waste yarn.

b) Piece Dyeing

Many of the rationalisation processes described above arise from ideas already in practice in continuous dyeing. A continuous dyeing plant for cotton or cotton/polyester piece goods appears a fearsome thing on paper and even more terrifying in practice, but it can be run simply and efficiently by paying sufficient attention to detail. Let it be quite clearly stated, no continuous dyeing plant can be run at all unless the material presented to it is thoroughly prepared so as to be fully and evenly absorbent in the shortest possible time.

Fig. 7

The continuous plant shown in the diagram is designed to run at speeds of up to 60 metres per minute. Let it also be quite clearly stated that one also requires a jig dyeing machine, a beam or jet dyeing machine to cope with those isolated instances of small yardages which may not be quite perfect, as up to 1,000 metres of cloth may have to be run through such a plant before the machinery can be correctly adjusted. Once this happy stage is reached however, large runs of cloth per shade are easily dyed and lots as small as 5,000 metres in length can be conveniently processed albeit at a slightly higher cost per metre.

The point to note about the machinery layout is that provision should be made at strategic points for A frames to permit batching at intervals, a necessary precaution in case of machinery failure or to enable routine maintenance to be carried out at separate times. There should be provision for interchangeable padding mangles to cope with cloth of varying widths, otherwise longitudinal lines will be visible on the finished cloth as a result of differential wear on the rollers of the padding mangle. There should be adequate and even pre-drying capacity in the infra-red and subsequent pre-drying section and of course a good thermostol capacity, capable of at least 220°C. Whether or not one chooses hot air or contact heat as the means

of heat transfer for the thermosol process is a matter for consideration but in general the contact heat method is preferable as the processing time is shorter due to the more rapid heating-up of the cloth and a more even distribution of heat can be achieved across the width. The constitution of the padding liquor is most important, it should be kept to the minimum possible containing the necessary dyestuffs in liquid form, migration inhibitor and wetting agent if necessary. All products in the padding liquor should be non-foaming if possible so as to avoid the abomination of anti-foaming agents as these lead inexorably to dyestuff aggregation and hence spots on the finished cloth.

The plant should be flexible enough to cope with cotton and cotton/polyester cloth dyed with vat dyestuffs, reactive dyestuffs, solubilised vat dyestuffs and sulphur dyestuffs combined as necessary and possible with disperse dyestuffs in the case of cotton/polyester cloth. The lay-out described will also cope with the one-bath pigment/resin system which is equally suitable for the dyeing of cotton or cotton/polyester cloth in pale shades.

Much attention has recently been paid to the development part of the range which is nowadays the pad-steam process. Recent improvements include modification of the classical pad-steam process to the wet-steam process developed by BASF where the hot flue is dispensed with as is also one padding mangle.

The goods are padded with vat dyestuff in the colloidal form and then with or without an air passage, the goods are treated in a dip trough with the chemical liquor and steamed for one minute in saturated steam and finished as usual.

Fig. 8

There are three different methods of installing the dip trough of which the best method is to use the trough as a water seal at the entrance to the steamer. Installing the trough outside the steam can have some technical and financial advantages however. A high liquor pick-up gives several advantages in this wet on wet process.

Fig. 9

The advantages of the modified wet steam process are savings in machinery and power, shorter cleaning times which brings greater flexibility for shorter runs and improved quality due to better penetration and levelling, with no migration problems because there is no intermediate drying process.

For reactive dyestuffs steam fixation is the normal practice but the cold-pad-batch fixation process is also possible on both cotton and cotton/polyester fabric. Cold-pad-batch fixation or better fed dyeing is also possible for 100% cotton using vat dyestuffs, with or without intermediate drying. This process utilises the rapid rate of exhaustion of vat dyestuffs in the cold, reference to which has already been made in connection with yarn dyeing.

Fig. 10

This is a semi-continuous process which can be carried out with or without intermediate drying. For fabrics that can take up a great deal of liquor e.g. terry towelling, twills and corduroys, the wet on wet process can be used, but for the more densely woven fabrics e.g. mercerised satins, poplins and fabrics made from regenerated cellulose intermediate drying is preferable. The minimum batching time is two hours but times of up to four hours are necessary in certain cases. Longer batching times than this although unnecessary do not result in any deleterious effects. The fabric must be fully absorbent and the dyes and chemicals correct in choice and quantity. Batching must be carried out thoroughly wet, particularly at the selvages of the material, and all air excluded from the batch during the fixation period. This latter point is most important as a partial vacuum develops within the batch as the oxygen is consumed during the reaction. Without tight sealing, more air will enter and cause oxidation stains. An efficient seal can be obtained by the use of a thin soft plastic sheet as the final wrapping of the batch, the ends of which are tied down onto separate strips of pre-wetted cloth wound round the beam at the edges of the batch. In the case of cotton/polyester materials the wet dyestuff used can be developed in a similar manner although in this case of course the material will have been pre-dried because of the prior thermosol process.

Other developments include attempts to achieve rapid fixation of vat dyes in hot, that is 90°C, aqueous liquors by using chemical reaction accelerators with e.g. a Williams type development unit.

Fig. 11

Not all vat dyestuffs are fully developed by this process however, and further work is necessary before one could make recommendations suitable for the development of all vat dyeing shades.

All these developments have the aim of reducing the time taken in processing and thus reducing costs particularly that of energy and increasing the production and quality. It has recently been reported ³ that savings of 500,000 to 600,000 btu's per 100 yards of goods can be made when dyes are applied by the pad-steam method compared with the pad-dry-bake or pad-dry-steam methods. Expressed in terms of fuel this means a saving of 2.2 gallons per 100 yards of dyed fabric, a saving in American terms of $\frac{1}{2}$ to 1 cent per yard at present prices.

OTHER MECHANICAL CONSIDERATIONS

After deciding on the basic machinery to be installed, be it for yarn or piece dyeing, there comes the question of deciding upon manual, semi or fully automatic control systems, and the use of ancillary systems such as instrumental match prediction. These points will be discussed with reference to batch-wise or yarn dyeing rather than with reference to continuous dyeing plant, as control systems in the latter case

are really an integral part of the machinery layout.

It is contended that semi automatic control e.g. system which has time/temperature control, automatic flow reversal, but requires some manual override, for example, for control of filling, emptying or rinsing is more interesting in the plant under discussion for many reasons. A semi automatic system is more flexible, relatively simple and is much less expensive, allowing more production machinery to be purchased for a given capital expenditure. A four beam package dyeing machine can cost approximately £55,000 together with a further £25,000 required for a fully automatic control system, compared to only £5,000 for semi-automatic control. This would mean that four production units in the semi automatic state could be bought at a cost of three fully automated units which is a very significant factor.

Similarly when considering instrumental match prediction and shade matching, it has to be considered whether this is yet far enough advanced to justify the high capital cost for installation and the running expenses, involving as it does the need for highly trained operating staff. It is submitted that attention to first principles, simplicity and good control of all operations will lead to good reproducibility of dyeing which is the main aim of such systems. It must also be remembered that any computer will only work within the framework of the information which is set to it. It is of little practical value to have recipes for yarn dyeing, e.g. which a computer predicts on the basis of an IW vat dyestuff shaded with an IN vat dyestuff when the reverse is a far better choice both technically and economically. Considerations

of this type must be the basis of dyestuff selection for all practical dyeing recipes. Instrumental match prediction is most useful where the shade range is under the direct control of the dyer, where the number of substrates is small and where the dyestuffs used show a high degree of exhaustion. Under these circumstances however, sufficient attention to detail will give good results without the use of instrumental match predictions.

This paper has been presented with the object of giving a broad outline of the modern approach to the dyeing of cotton and cotton/polyester blends. If it has raised questions in addition to those which it has answered then it will have achieved an additional definite purpose, as it is held as a principle well worth re-stating that the technical approach to the dyeing of textiles is the most beneficial approach. Commercial viability must of course be an important factor but this should be judged in the light of the technical expertise available for the dye user, from the dye manufacturers, machinery suppliers, fibre producers and other advisory sources.

Fig.1

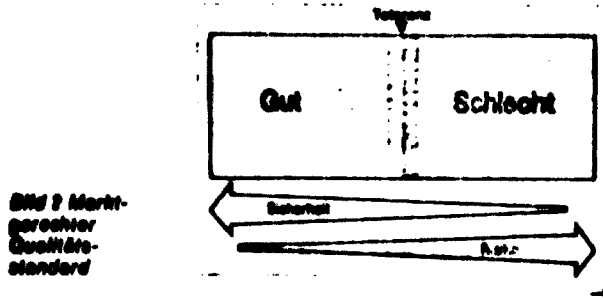


Bild 2 Marktgerader Qualitätsstandard

Fig.2

Praxisüblicher Zeitaufwand für Küpenfärbungen

Teilprozesse	Kontinuierlich min	Diskontinuierlich min
Aufbringen des Farbstoffes	0,15	30
Fixieren	1,0	30
Spülen	0,5	30
Oxidieren	1,0	15
Seifen	1,0	20
Spülen	0,25	10

Fig.3

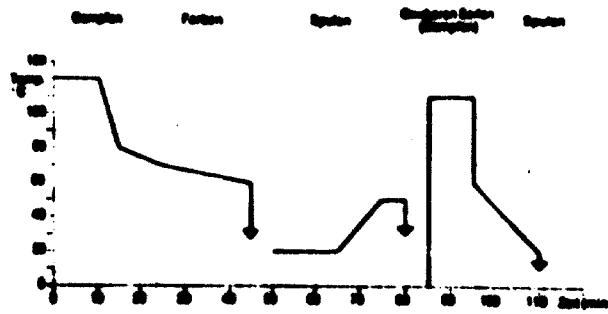


Bild 4 Optimiertes Färbeverfahren für Indanthronfarbstoffe

Fig.4

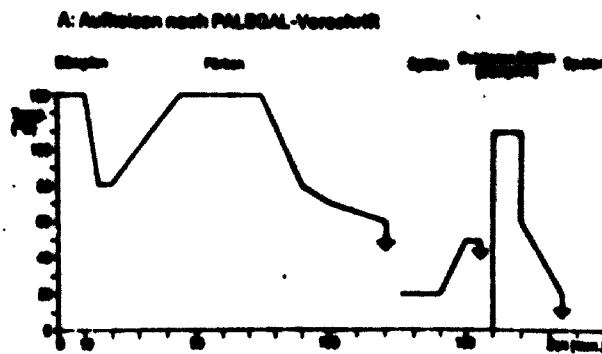


Bild 5 Optimiertes Färbeverfahren für Collocotronfarbstoffe /

Fig.5

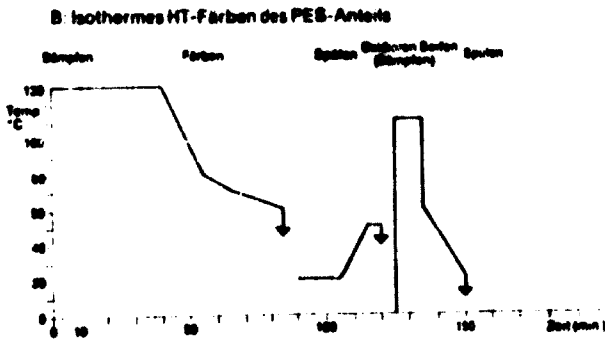


Bild 6 Optimiertes Färbeverfahren für Collestrenfarbstoffe II

Fig.6

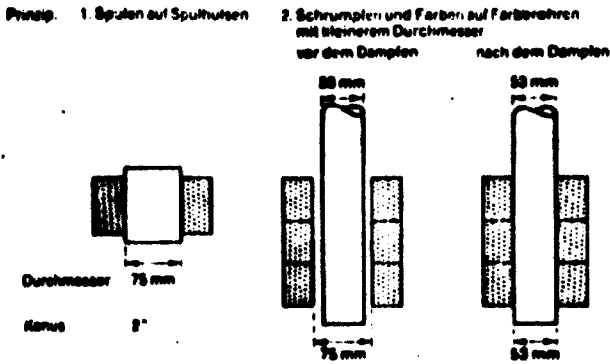


Bild 7 Vorschrumpfen von zylindrischen Färbespulen auf PES/ GEL-Mischgarn

Fig. 7 (a)

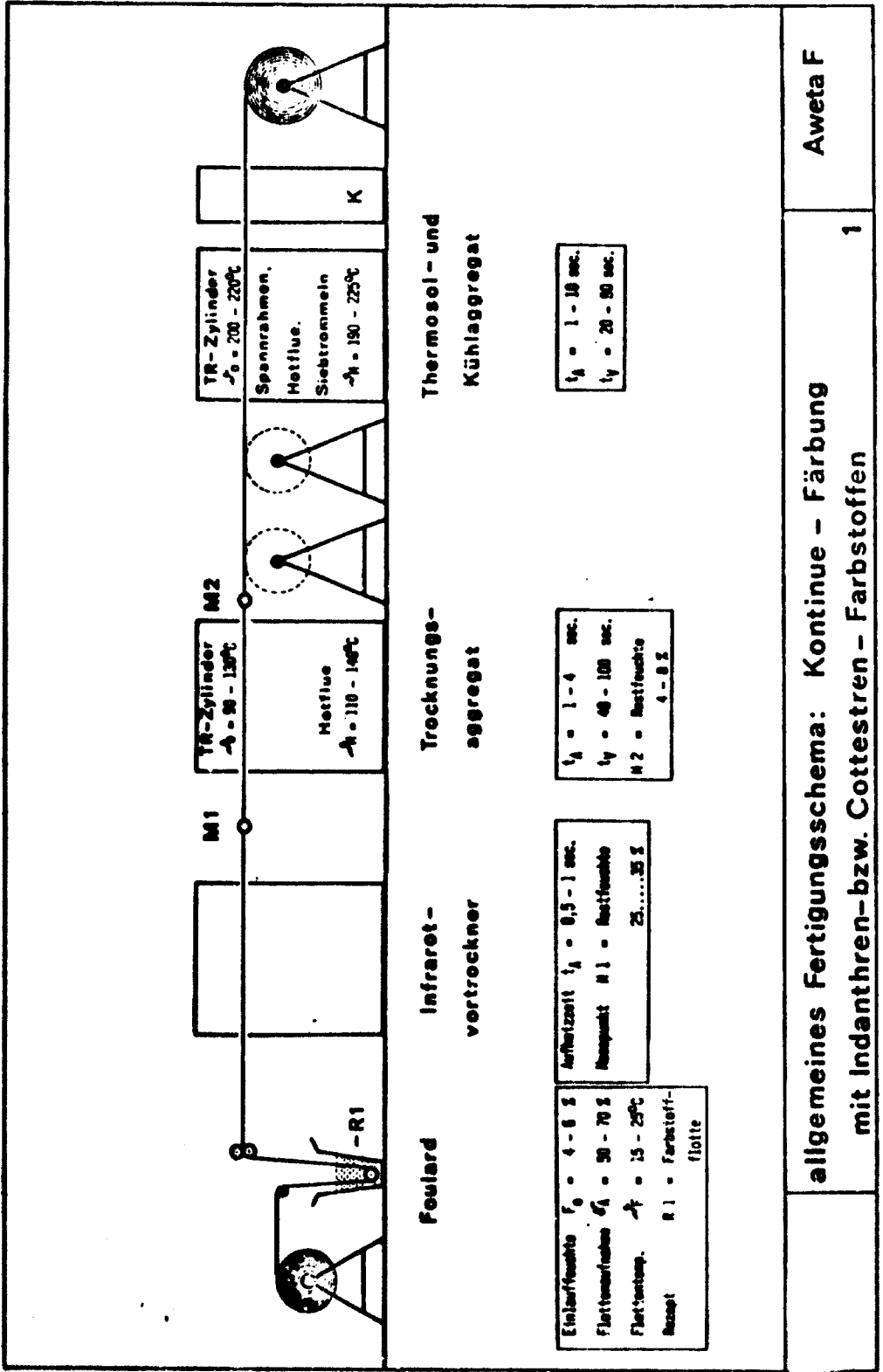


Fig. 7 (b)

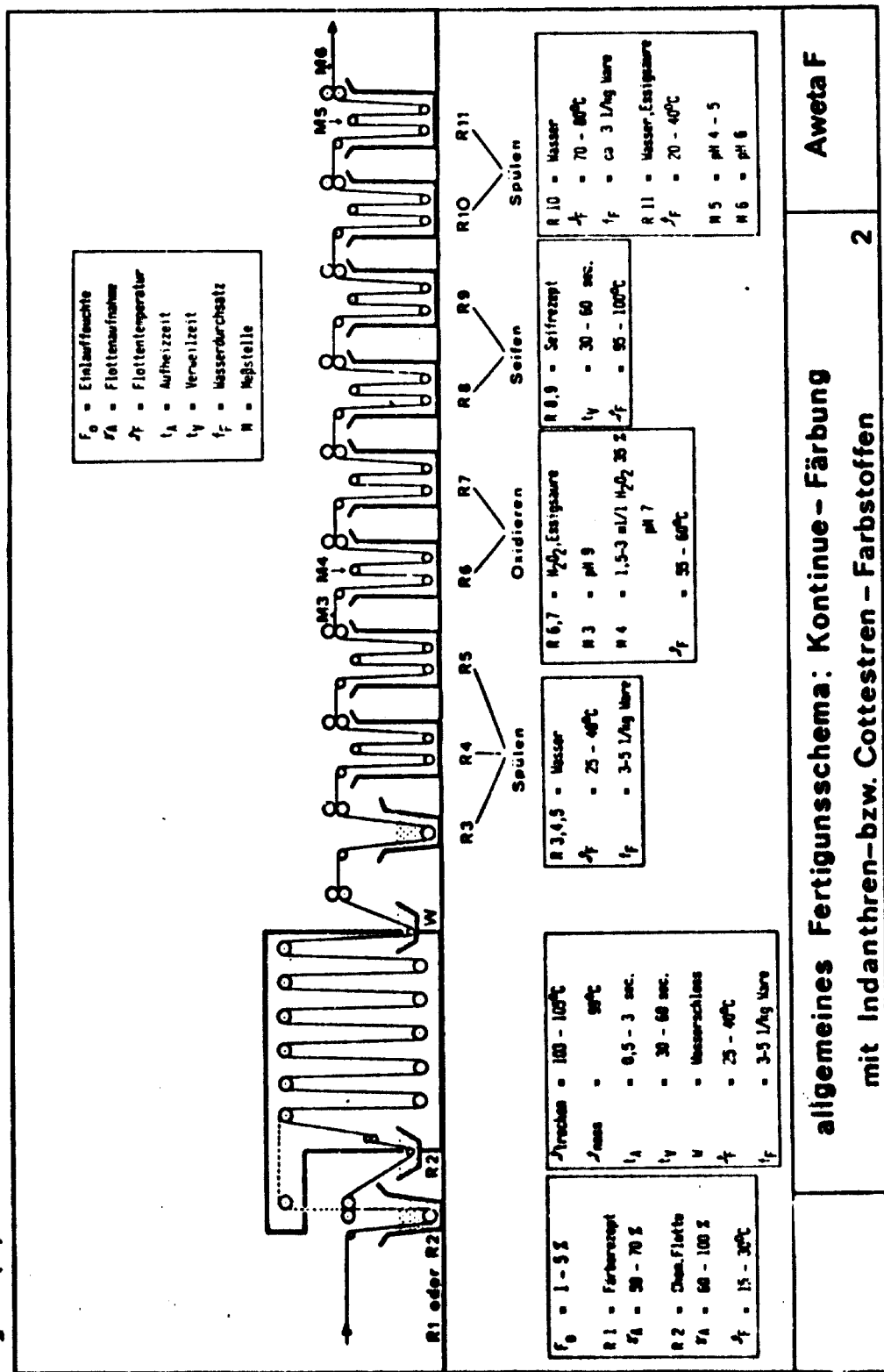


Fig. 8

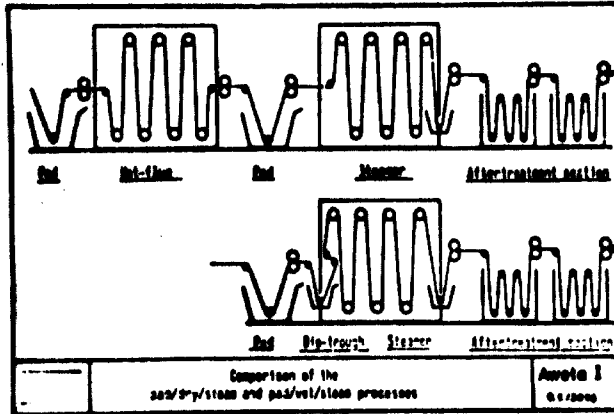


Fig. 9

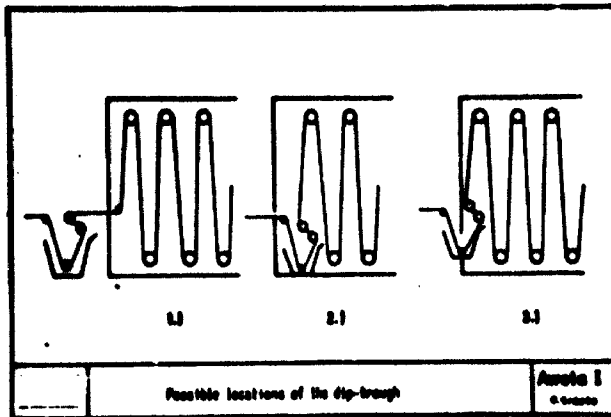


Fig.10

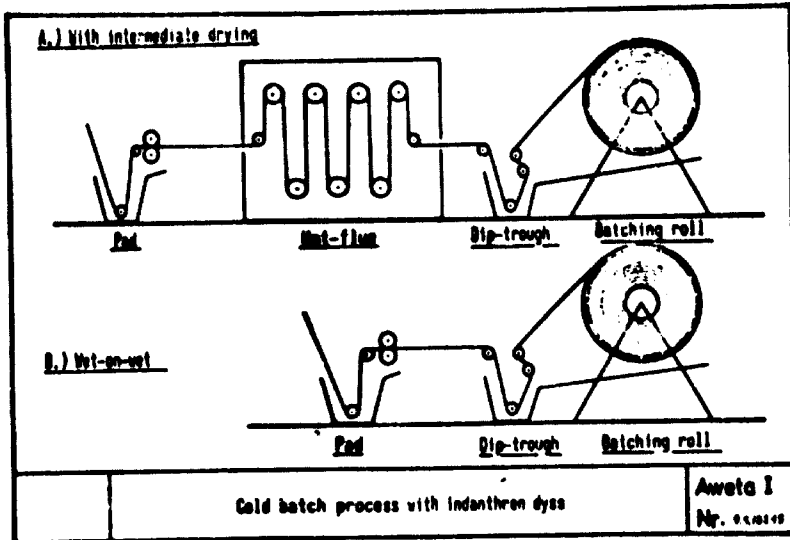
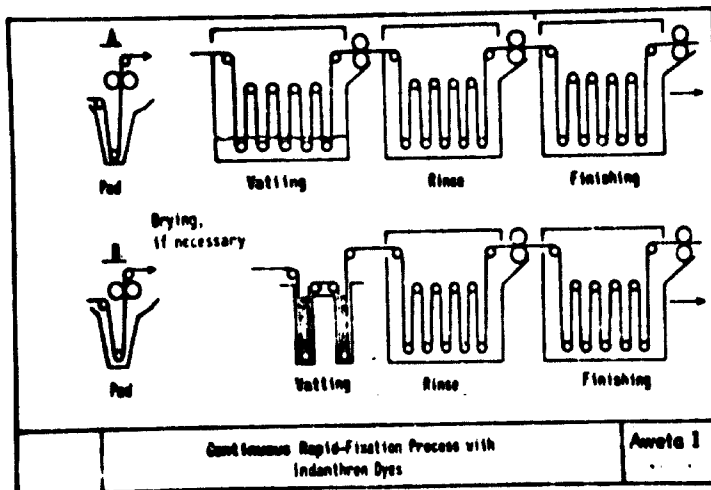
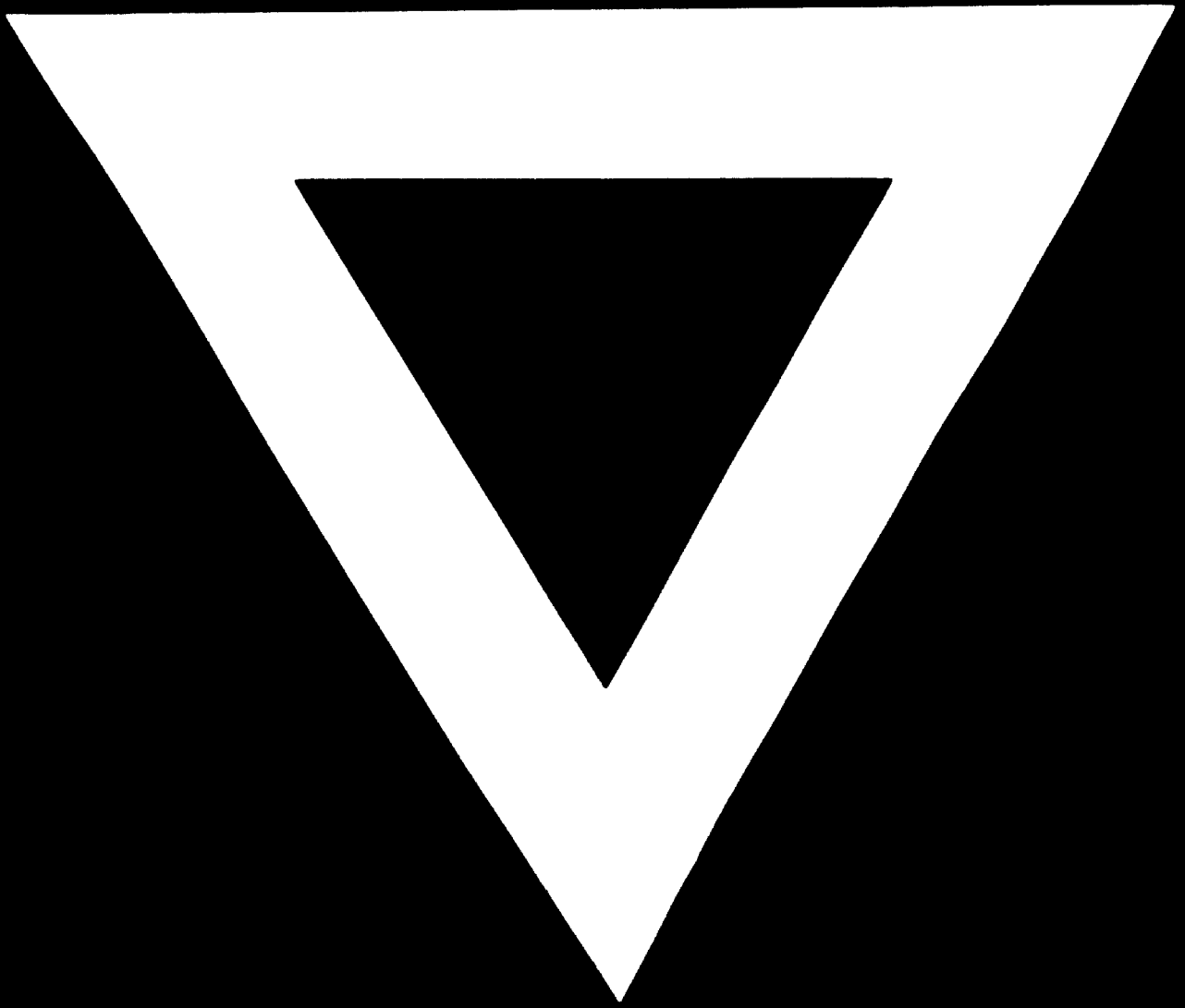


Fig.11





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