The Complete Book on Textile Processing and Silk Reeling Technology
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Textile industry in India is the second largest employment generator after agriculture. It holds significant status in India as it provides one of the fundamental necessities of the people. Textile processing is one of the important industries related with textile manufacturing operations. It is a general term that covers right from singeing to finishing & printing of fabric apart from giving huge value-addition at every stage of processing. A number of new innovations have led to the industrialization of the textile industry. The silk reeling techniques are excellent methods to produce superior grade raw silk which is used by the textile industry to produce exotic fabric. Silk reeling is the final and purely commercial phase of sericulture. It is concerned with unwinding of the silk filaments of the cocoon. The sericulture industry is agro based and flourishing mostly in rural areas. More than 50 per cent of silk is reeled by a villager using country charka which forms the cottage industry. Silk provides much needed work in several developing and labour rich countries. The textile industry is primarily concerned with the production of yarn, and cloth and the subsequent design or manufacture of clothing and their distribution. The raw material may be natural or synthetic using products of the chemical industry.

Some of the fundamentals of the book are chemical modification of textile cellulosics, fabric varieties, silk as a textile fibre, silk reeling technology, silk re-reeling technology, fluidized beds to textile processing, high alpha cellulose pulp for viscose rayon, reaction of cellulose with cross linking agents, textiles adhesives, flame retardants for textiles, halogenated flame retardants, antimony and other organic compounds, surfactants, chemical used in textiles, etc.

This book contains fabric varieties, silk reeling technology, cellulose ethers, crease resistance of cellulose textiles, tone and shade control in textile, textiles adhesives, flame retardants for textiles, chemical used in textiles. This book will be resourceful to upcoming entrepreneur, Seri culturist, existing industries, technical institutions etc.

Content:
Sample Chapter:
Chemical Modification of Textile Celluloses

Cotton cellulose is a linear polymer containing hundreds of interlinked glucose units through oxygen bridges. It contains both primary alcoholic groups (\(\text{CH}_2\text{OH}\)) and secondary ones (\(\text{CHOH}\)), and from the chemical point of view, one would expect cellulose to behave like alcoholic compounds. However, when one thinks of cellulose from the point of view of textile end use, he is confronted with a number of limitations. Such limitations arise out of the necessity to maintain practically all the textile properties that cellulose normally possesses. For instance, the chemical treatment must not alter the tensile strength, which is believed to depend on chain length and intermolecular cohesion; secondly the treatment should not adversely affect the moisture relations of cellulose; thirdly the elastic properties which make spinning possible should not be destroyed; and lastly the treatment should affect useful textile properties, such as dye-ability, handle, drape, lustre and softness.

In the ultimate analysis, all the above limitations involve a through understanding of the physical structure and chemical properties of textile cellulose. Fortunately, thanks to the numerous pioneering researches conducted during the last fifty years or so, a fund of knowledge is now available which makes discussion possible. Modern fibre science has made great strides as a result of the impetus received through the synthesis of new chemical fibres. At one time it was considered that 'king cotton' will have to lose ground to modern synthetic fibres. But it was soon realized that, if starting from raw materials like coal tar or petroleum chemicals, which have no relation whatsoever with fibrous properties, one could synthesize such valuable fibres as nylon or terelyne, one could as well start from cotton, flax, ramie, or jute and look forward to many and far reaching results. This view has gained considerable support during the last ten years.

Structure of Cellulose

All textile materials are linear polymers characterized by the presence of long chain molecules possessing polar side groups, such as OH, NH\(_2\), etc., with residual valencies. The long chains are arranged in a remarkably orderly fashion and are held together by Van der Waals forces, hydrogen bonds or salt linkages between acidic and alkaline polar groups of adjacent molecules. In textile celluloses, the chain length varies from 300–600 glucose units (regenerated fibres) to 3,000–7,000 or more glucose units (natural celluloses). The cohesive forces between the side chains are due to hydrogen bonding between the hydroxyl groups of adjacent chains. In some places, along the length, these chains are packed together in a rather rigid and orderly fashion. These regions are called 'crystalline' regions and are believed to contribute mainly to the tensile strength and chemical stability. Further, these molecules are generally oriented towards the fibre axis. The degree of such orientation plays an important part in the tensile behaviour of cellulose. In other regions, the packing of molecules is not orderly; these regions known as 'amorphous' regions are believed to be more easily accessible to moisture, dyes and other chemicals. They may also account for the elasticity and extensibility of textile fibres.

The following points are worth recapitulating: (i) the chain length and degree of orientation contribute largely to the strength and other tensile properties of textile celluloses; (ii) the manner of random packing of molecules in the 'amorphous' regions of cellulose determines its accessibility to all outside chemical agencies. Chemicals having a molecular size greater than the molecular voids in the amorphous regions cannot enter them and hence cannot bring about easy chemical transformation; (iii) the alcoholic nature of polar hydroxyl groups in cellulose makes possible reaction between cellulose and alcoholic groups, resulting in reactions, such as etherification, esterification, xanthation, oxidation, etc., and (iv) chemicals having strong hydrogen bonding properties have an affinity for cellulose and can bring about changes in the physical properties of cellulose by altering the nature of packing of different chains (mercerization) or by
clinging on to them and then adding to themselves until the size of the agglomerate becomes so big that a removal, by reversal, of the effect is made difficult.

These ideas can be made clear by reference to Figs. 1 and 2, which show the unit residue from which cellulose is built, the manner in which molecular chains cohere in the fibre and the manner in which they are packed.

There are two ways in which the subject can be viewed. Cellulose may be considered as a linear polymer containing a number of hydroxyl groups which make a variety of typical chemical modification possible. One might then list together all the type reactions under suitable categories, e.g., esterification, etherification, oxidation and xanthation, and consider the different useful properties resulting from such reactions. Alternatively, cellulose may be considered as a fibrous material exhibiting a number of useful or defective textile properties and then consider ways and means of chemical modification with a view to rectifying the defective properties. The objective of this paper is to focus attention on what has been done or can be done to improve the textile properties of cellulose by taking recourse to chemical modifications.

**Property of Textile Cellulose**

The following are a few of the numerous textile properties of cellulose: warmth; drap; resilience and drape; elasticity and strength lustre; crease-resistance; dimensional stability; spinnability; abrasion and flex resistance; heat, sound and electrical insulation; quick drying; water repellency; air permeability; resistance to mildew and rot-proofness; absorbency; wash resistance; and soil resistance.

The relative importance of one or more of these properties, however, varies from country to country, climate to climate and dress habits of different people. Moreover, it is ultimately the end use that determines the exact manner in which one or more properties are selected or modified. However, the properties can be broadly grouped under the following headings:

- Properties based on polymer structure—(i) elongation and elastic properties; (ii) flex resistance, tear strength and wear life; (iii) wet strength, dimensional stability and wash resistance; (iv) crease-resistance and drape; and (v) bulk density and warmth.
- Properties based on form, dimensions and surface characteristics of fibre—(i) lustre; (ii) slipperiness and clinging resistance (iii) resistance to soiling; and (iv) permeability.
- Properties based on hydrophilic or hydrophobic characteristics—(i) Water repellency; (ii) absorbency; (iii) quick drying; (iv) electrical insulation; (v) dye-receptivity; and (vi) moisture regain.
- Properties based on structure—(i) mildew-and rot-resistance; (ii) resistance to deterioration by light, heat, chemicals, etc.; (iii) flame resistance; and (iv) ion-exchange properties.

**Elongation and Elastic Properties**

Almost any treatment which changes the molecular packing in cellulose will have a significant effect on these two properties. The simplest and the most striking example is treatment of cotton yarn under tension with steam, whereby the elongation is considerably reduced; such destretched yarns find commercial application in the manufacture of improved tyre cords. References to literature are too numerous to mention here, but a process developed at the Shri Ram Research Institute three years ago is worth mentioning. The yarns were dipped in a mixture of amyl and butyl alcohol for a short time and then stretched and steamed to remove the solvent. Increase in tenacity of the order of 50–80 per cent was recorded. Unfortunately, the method could not be utilized commercially due to various considerations.

Another example of a simple chemical treatment which altered the elastic properties of cellulose comes from the Southern Regional Laboratory in U.S.A. Bandage fabric was mercerized in caustic soda washed and dried without tension. Such bandage has more desirable properties and a much higher elongation (35%) than untreated material. It fits the various parts of the human body more efficiently due to
its elastic nature.

A third and extremely important chemical method of altering the elongation and elastic properties of cellulose is by reaction involving the use of cross bonding agents.

**Flex Life, Tear Strength and Wear Life**

It is being more and more realized that changes in the crystallinity of cellulose can be brought about by chemical means. Segal et al. treated native cotton with aliphatic amines and obtained cottons with varying degrees of crystallinity. It was thus possible to bring down the crystallinity from 90 to as low as 25 per cent. The treated cottons show altered dyeing properties, improved chemical reactivity, better flex life and improved tear strength. Further evaluation of such decrystallized cotton had been handicapped by lack of enough treated material for test purposes. It appears, however, that Greathouse et al. have succeeded in trying the process on a pilot plant scale and increasing developments may be expected in the near future.

**Wet Strength, Dimensional Stability, Wash and Crease-Resistance and Drape**

All these related properties have assumed importance since the introduction of regenerated cellulose fibres, and have been largely improved by cross bonding and by aminoplast resin modification. Considerable attention is being directed towards the treatment of cotton in this way, and the introduction of silicon resins and nitile lattices along with the conventional urea-formaldehyde or melamine-formaldehyde resins need special mention here, as they seem to overcome some of properties to a significant extent.

Though drape is associated with yarn and fabric construction, it would appear that decrystallization and cross linking could improve these properties to a significant extent.

**Bulk Density and Warmth**

These properties do not appear to have received as much attention as they deserve. It would perhaps be safe to assume that these two properties are inter-related and that warmth can be increased by changes in bulk density. In an excellent review on the thermal properties of textiles, Morris lists a number of physical factors that contribute to the thermal characteristics of textiles, such as specific heat, bulk density and conductivity. However, there appears to be little work done on the chemical modification of cellulose from this point of view. An interesting development for improving the heat retaining properties of textiles is the use of metallic flakes in the binding polymer sprayed on the surface, followed by baking. It is claimed that the fabric retains its permeability and at the same time, due to cloth shrinkage, the trapped air aids insulation. In a country like India, attempts to make cotton more warm may prove useful in the long run.

**Lustre**

So far, chemical methods to enhance lustre have been restricted to the use of mercerization. There have been numerous investigations on caustic mercerization and the latest series of papers by Fourt et al. are worthy of mention. The treatment of cotton with a strong solution of caustic soda changes the crystal structure of cotton cellulose from cellulose I to cellulose II (Fig. 3 and Table 1). The factors involved in the development of lustre have been summarized by Marsh.

![Fig. 3. Unit cell of cellulose I](image)

There have been notable contributions in the resin treatment of textiles with a view to obtain permanent lustre. In all such processes, the materials are treated with resins, dried and schreinered or calendared, and then cured. The effects obtained are made wash resistant.

**Fabric Varieties**

**Outline**

**What Does Fabric Mean?**

The fabric is a cloth material, which has the warp (vertical yarn) and the weft or filling (horizontal yarn) crossing each other at right angles. Though all fabrics may appear very much similar at one glance,
there are various cloth varieties, which have absolutely different patterns. For example, there is lace material and vertical knitwear cloth, in which the cloth material is formed only by intertwining the warp with the warp on the left and right mutually. There is also horizontal knitwear material in which the cloth is made by one thread making its way in zigzag direction horizontally, while forming a net continuously. Another way is to make felt cloth, in which the wool fibers are overlapped flat on each other and while rubbing them under heat, alkali and pressure, they are turned into felt.

Special Terms Related to Fabrics

(a) Selvedge

The fabric has slightly tightened part at the edge, with a width of 3–5 mm on both sides all through its length. This is called as the Selvedge of the fabric. The warp used for selvedge is called as selvedge yarn. As against the selvedge, the other part of the fabric excluding the selvedge is called as Ground. Both the sides get stretched while fabric manufacturing, dyeing and arranging etc. and they can get easily torn. Therefore, in order to give it additional strength, the warp slightly thicker than that of the ground is used or the warp same as that of the ground is arranged in double and used as one warp. Therefore, the selvedge part tends to be slightly thicker than the ground part. When the ground is a plain fabric or a figured texture fabric etc., many times the plain fabric or figured diagonal fabric is used only for the selvedge part. In the silk fabrics and woolen fabrics, a special pattern or a yarn of different color is used for the selvedge part. This also serves the purpose of decoration and design. Moreover, the woolen fabrics have the trade-mark or manufacturing company name woven on the selvedge. This is commonly called as selvedge mark.

(b) Width

The width of fabric is decided according to the purpose of its use following the custom for each variety. For example, the fabric for the inner lining material of kimono (Japanese style dress material) is said to be of less width. It is of about 36 cm and the belt material is about 30 cm in heavy belts. In round belts, the standard width is about 68–69 cm. In the export fabrics, usually the fabric is about 2–3 times wider than the inner lining material. The fabrics, which have double or triple the width of inner lining material, is called as double wide fabric, triple wide fabric respectively. These are called in general as wide fabrics. When the fabrics for special use have extremely narrow width, they are called as narrow fabrics. However, this is just a conceptual classification and there is no clear numerical boundary drawn anywhere. The width of woolen fabrics is usually 154–158 cm (60–62 in) but its ground is mostly of about 76–91 cm (30–36 in) in all varieties of the fabrics.

While showing the width, when the width is to be shown excluding the selvedge, it is called as Within Selvedge. When the selvedge is included in the shown width, it is called as Over-all.

(c) Length

While weaving a fabric, usually 5–10 reverse parts are taken as one length and the weaving is done. But, the length of one roll (91 piece) sent to the market as the product is as per the trading custom. The standard length of one roll of silk or artificial silk fabric is 45.72 m (50 yds), cotton fabric is 27.43 – 45.72 m (30 – 50 yds), the carded woolen fabric is 50 – 55 m, spun woolen fabric is 40 – 45 m and the hemp fabric is 55 m (60 yds). The cotton fabric used for internal lining of kimono is about 10.6 m long. The silk fabric (silk crape etc.) have 11.4 m as 1 reverse. However, each fabric variety tends to get a little longer successively.

(d) Density

The degree of density of the warp and the weft has a great impact on the texture and appearance of the fabric. It is one of the important conditions in determining the name and usage of the fabric. The degree of this density shows the number of warps and weft in the fixed section. The method of taking this section depends on the variety of the fabric and on the country. Each country has its own custom but generally, the number of threads between 2.54 cm (1 in) or between 1 cm etc. is shown. But, sometimes, the total number
of warps and wefts between a square inch is also shown.

(e) Weight (Momme)

Momme (=0.132 oz) is used as the unit for showing the weight (indirectly, it also means thickness) of the fabric per unit area. The origin of the Momme is the unit showing the weight per fixed area of the fabric. The fabric with 3.788 cm [cloth measure 1 Sun (=1.193 in)] width, 22.727 m [60 Shaku (=0.994 ft)] length and 3.75 gr weight (1 Momme) is said to be of 1 Momme. The fabric of the same area and weight 18.75 gr (5 Momme) is said to be of 5 Momme. The Momme is a special unit used only in Japan. Today, it is used only for the habutae silk and crepe silk in the silk fabrics and not for the other fabrics. The usual method of showing the weight per unit area of the fabric is to use gr number per square m for all the fabric varieties. In case of woolen fabrics, the width is fixed to be 60–62 in. So, since long it has been the custom to use the expression telling how many ounces it is from the number of ounces per 1 yd length.

(f) Mix Spun Fabric, Mix Woven Fabric and Graded Fabric

The fabric is either mixed spun or mixed woven, depending on the variety of yarns used for warps and wefts. Mixed spun fabric has the mixed spun yarn used for a part or whole of the warp and weft. The mixed woven fabric has yarn of mixed strands (ply) used in a part or whole of the warp and weft. The fabric, which has yarns of different kinds of fibers used for the warp and weft or the fabric, which has yarns of different kinds of fibers combined and woven in stripes partially in the warp and weft is also called as mixed woven fabric. When it is said ‘mixed weaving’, it always means that it is a fabric with yarns of different varieties of fibers. If the fabric is arranged with stripes of thick and thin yarn made from the same fiber variety, it is called as graded fabric.

(g) Tone, Texture and Flavor

The fabric differs in hardness, softness, smoothness and stiffness (flexibility, which gives a feel that there is something at the core of the fiber) depending on the combination of various conditions such as, the physical properties of the fiber that makes up the fabric, the yarn thickness, the twisting strength, the pattern of fabric, th density and the finishing method etc. The feeling that one gets after touching the fabric or the feeling that one gets after seeing its appearance, when it is worn as clothes, is also different in case of all fabrics. The condition of these feelings is shown by the words Tone, Texture and Flavor. These are mainly special terms, which show the complex feelings. The goodness or badness of tone or texture is an important element while judging the value of the fabric. This cannot be measured mechanically and it cannot be shown numerically. The person, who handles the fabrics, touches the fabric and judges the goodness or badness of it form his experience of several years.

(h) Sharimi

This is a slang word used in the trading world, when the tone of mainly the carded woolen fabrics is to be shown. When one picks up the fabric with a pointer, it has a touch of ‘shari’ (rustling).

(i) Sliminess

This is also a slang word showing the touch of carded woolen fabrics. This term shows the extent of goodness or badness of the woolen fabrics, which give a feel of slipperiness.

(j) Bulkiness

When the yarn or the fiber gives a feeling of bulkiness, when it is held in hands, it is called as Bulky. Apart from the elasticity of fiber, this property varies according to the pattern and finishing method of the yarn or fabric.

(k) Draping Quality

When the fabrics are worn on the body as clothes or when they are hung down like a vertical curtain, the loose part sags down and it shows a curved line. This condition varies according to the variety of fabrics. The main elements, which cause this, are fiber weight, stiffness, flexibility, surface smoothness, yarn twists, density of fabric, condition of pattern and finishing. All these different conditions can be
generalized under one name as Drape quality. This quality is one of the important properties for deciding the clothes decoration value in the material for ladies dresses.

(I) Crape

Sometimes the fabrics are woven by using firmly twisted yarn for the weft (sometimes, for both warp and weft) and the twists are reversed in alternate yarns, inserting one thread twisted clockwise and the next anticlockwise. Thus fine creases are made to occur on the surface of fabric when the yarn shrinks after weaving. These creases are called as Crape. For example, the creases seen on cotton crepe or crepe silk.

(m) Moire

If two fabric sheets are piled on each other and if we look through them while shifting that piled position suitably, we can see inconsistent light and darkness like the film of wood grains. These are shown because the reflection condition of see-through rays changes due to the piling of tall parts and short parts of the warps and wefts floating on the fabric surface. This is called as Moire. In order to settle this on the fabric surface, two sheets of fabrics are piled up in a position so that they will show the moire and they are passed between rollers. While heating, they are given pressure. Due to this, the taller parts on the surface get pressed to a large extent and become flat. Therefore, the rays are reflected on flat surface according to the parts and those parts look very white. Further, there is also a method of setting the moire, in which a film resembling the moire is carved on the surface of the roller and the process of pressing is carried out with it on the surface of the fabric. On the contrary, when plain dyed fabrics, especially plain black dyed fabrics, are to be given a calendar finishing, the moire film is seen unnecessarily and it spoils the appearance of the product.

(n) Wash and Wear

Generally, the synthetic fibers have very little moisture absorption rate. So, when the shirts and dresses made with them are washed, even without starching them, if they are taken out from water and hung up without wringing, the water gets drained naturally. The clothes get dried very fast. They do not get wrinkled and so ironing is not required for them. They can be worn immediately. The term Wash and Wear (abbreviated as WW) means ‘wearing immediately in the washed condition’.

Fabric Patterns

(1) How to Show the Pattern

The mixed status of warps and wefts, which make up the fabric, is called as the pattern. Even if the fabric is woven with the same yarn, its strength, appearance and tone changes according to the weave (interlacing pattern).

The pattern of the fabric is shown with the pattern diagram. The design paper is used to draw the pattern diagram. The section 1. inserted between the two ruled lines in vertical direction, shows 1 warp. Similar section in the horizontal direction shows one weft. For example, in Fig. 1, (a) each of 1, 2, 3 ... is the warp and each of i, ii, iii, ... is the weft. The design paper should have one bold line drawn after every 8 lines.

For the relation of the vertical and horizontal, usually the squares are used (this is called as design paper of 8¢ 8). However, in the fabrics with figured texture, when the fabric having different thickness of warp and weft is to be designed, the paper having section lines of the width proportionate to the thickness of the yarn to be used, is taken (For example, the paper shown in (b) of Fig. 1. This is called as design paper of 8¢16). In short, if the paper proportionate to the thickness of the warp and weft is not used the scale of the designed pattern and the scale of woven pattern will be different. As seen from the table, the method of drawing the pattern drawing is to color the warp in black (or other color). The places, where the warp crosses over the weft are also colored in black.

The relation of the two is as shown in Fig. 2. In it (a) shows the actual state of the fabric. When this is seen from the lower side of the diagram, its cross-section looks like (b) and when it is seen from the right
The side of the diagram, its cross-section looks like (c). The fabric of such a pattern can be shown in pattern drawing, as shown in (d). (The part painted with slanting lines shows 1 complete pattern.) In this case, it is seen that the warp and weft are taken up and down one by one and the interlacing is done.

However, sometimes, depending on the pattern, there is also one warp crossing over two or more wefts continuously in the pattern drawing. Again, while drawing the pattern drawing, the beginning is usually done from the first hole at the lower end on left side. For this point, the place where the warp crosses over the weft is taken as the cardinal point. Normally, the direction of warp and weft is shown with 2–3 circles drawn.

Fig. 2 Plain weave pattern

(2) Varieties of Patterns

(a) Basic Patterns

There are unlimited varieties of patterns but there are three basic varieties, such as Plain weave, Twill weave and Sateen weave. All the other patterns are either the variations of these three basic patterns or a combination of them. These three varieties of patterns are called as the 3 basic patterns of fabric.

(i) Plain weave: Plain weave is the simplest of all fabric patterns. The warp and the weft are crossed over each other one by one alternately up and down and they are interlaced. It is as shown in Fig. 2. In this pattern, the crossing length of both the warp and weft is stopped at minimum. So, the texture is tightly close. This pattern makes a very strong fabric. This pattern is widely used for the fabrics used daily, such as cambric, yukata material and habutae etc.

(ii) Twill weave: Twill weave, as shown in Fig. 3, has the warp of 1 float over the weft of i and it sinks under the weft of ii, iii. Similarly, it floats over the weft of iv and then sinks under v and vi. Such floating and sinking is repeated.

The position of mixing warp of 2, 3, ... with the weft is only shifted in sequence one by one and the floating and sinking similar to 1 is repeated. Accordingly, in twill weave, the point of warp floating is seen in slanting line on the surface of the fabric. This is called as slanting line. The surface on which this line runs from lower left towards upper right is called as the right side of the fabric.

The twill of Fig. 3 is called as 1/2 Twill and the twill of Fig. 4(a) is 1/3 twil, (b) is 2/2 twill and (c) is 1/2 1/1 2/1 twill. Apart from this various combinations can be made in twill weave. The most commonly used patterns is 1/2 and 2/2.

In the display method of twill pattern, the horizontal line is considered as the lowest end weft in the pattern drawing.

The warps are counted from left side and the number, which floats over this weft, is written as numerator. The number sinking below this weft is written as denominator. Thus the status of one cycle of floating and sinking is shown in number. This is a common method of displaying twill-weave pattern in most of the countries. Besides, when it is necessary to show the direction of the slanting line, it is marked with arrows such as 1/3 or 2/2.

In twill weaving, if the floating length of warp and weft is longer than that of plain weaving, only the pattern of fabric is loosened. Thus, the strength of fabric is reduced to some extent.

(iii) Sateen weave: In this pattern the structural points, between the warp and the weft, are made very few. These structural points are also dispersed so that will not be continuous. The fabric surface has either only the warps floating on it or only the wefts floating on it. The fabric with only the warp floating, is called as Warp sateen and the fabric with the weft floating, is called as Weft sateen. In the sateen pattern, the floating yarn covers the structural point and so it is almost not seen. Therefore, the surface is smooth and lustrous.

The characteristic feature of sateen is that since the texture is loose, it is soft to touch. The sateen pattern has varieties also. There are fabrics in which 5 warps and wefts taken at each time and the pattern
is completed. Some fabrics have 8 of them at a time and some have 12 at a time. These are respectively
called as 5 ends of shaft sateen (It means weaving the fabric using 5 warp threads), 8 ends of shaft sateen
and 12 ends of shaft sateen.

Figure 5 shows the pattern, of 5 shaft sateen with 2 cycles of warps and wefts. (a) is the state
showing the actual fabric from the black side, (b) is the cross-sectional state showing this from the lower
side, (c) is the cross-section state showing it from the right side and (d) is its structural diagram. Figure 6
shows the structural diagram of two cycles of 8 shaft satin and Fig. 7 shows one cycle of 12 shaft sateen. In
it (a) is the state seen from its lower side and (b) is the state seen from its right side. As seen from the
structural diagrams, the sateen pattern has the floating point of the same warp only at one place in one
cycle (one complete pattern).

This structural point is arranged at a fixed distance following the rules. This distance (gap) is called
as the skipping point of the satin pattern.

For example, in the 5 shaft sateen, the warp 2 floats over 1, 3 over 2, 4 over 3 and 5 over 4. From
these positions, each one floats on the weft shifted after every two yarns and so the skipping points are 2.
Figure 6 and Fig. 7 show that the skipping points in them are 3 and 5 respectively. So, similar to the case of
5 shaft sateen, if the structural point is made at the point, where the wefts are shifted at every 3 or 5 yarns
sequentially, a complete pattern can be done.

As a basic principle while drawing the structural diagram of sateen, the surface, which has few points
with the warps floating over the wefts, should be at the top in the drawing. Accordingly, in case of warp
sateen, as shown in Fig. 7 the status, seen from the back of the fabric, is drawn. While weaving also, the
weaving is done while keeping the backside upwards. The reason for this is that, the number of holes to be
painted is less in the structural diagram while drawing. Besides, during the weaving, the number of warps
lifted up for opening a shed, is less. So the lifting force can also be saved.

Due to the same reason as in case of sateen weave, while weaving the material for figured fabrics,
the whole fabric is woven in reversed status. Therefore, in these cases, when the fabric is in the machine
front surface is actually the backside of the fabric.

Silk Reeling Technology

The single filament from the cocoon cannot be used for any purpose as it is too fine (2 to 3 denier).
Hence based on the denier of the silk yarn required to be produced for any particular end use, a known
number of filaments are combined and unwound together to form a single compact raw silk yarn. The
unwinding of the filaments from softened cocoons in a water media, combining the filaments and winding
the same onto a spool or reel is called reeling.

Softened cocoons are brushed to detect the end of the filament after which they are transferred to the
reeling basin for unwinding the filaments. New filaments are added or joined to the existing filaments in the
group, as and when any filament breaks or the filament in the cocoon is unwound completely, so that
continuous raw silk yarn of a required denier is obtained.

History of Silk Reeling Machines

In the very beginning, silk from cocoons was spun into yarn; like cotton. Later the hand spinning
wheel was developed where the reel—a square drum was rotated by one hand and the other hand was
used for twisting and joining the cocoon filaments. The cocoons were boiled in a pan near the equipment.
Development over this equipment was another hand reeling machine with a large reel of 75 cms
circumference connected to a handle for rotation. The reeler operated the handle with one hand and
simultaneously drew and twisted the filaments with the other hand.

In a further development, the reel circumference was reduced and other components such as a
distributor, thread guide, 'V' shaped brackets for introducing croissure were developed. The cocoon
softening procedure was also changed, with the cooking vessel embedded in a hearth. The number of skiens made was also increased to two.

During the 17th and 18th century, silk reeling machines underwent a lot of changes for improving the quality and also increasing the production of silk yarn. New reeling machineries were designed and developed such as the Italian systems, French systems and Rotellino Galbiste systems of reeling.

In these reeling systems, reeling was direct to form hanks so that they could be directly used for winding and twisting operations. The machinery included automatic brushing arrangement, jetteboutte assembly, button to combine the filaments together and croissure for agglutination of filaments. The large standard reels were enclosed with a built-in heating arrangement for drying the raw silk hanks.

In the Italian system of direct reeling, the filaments were twined within itself, i.e. the tavelletta type of croissure was adopted. The agglutinated filaments were drawn behind the reeler and wound on to the reels placed about 2 mts away. The agglutination of filaments in this method was advantageous as the reeling end was coiled with itself and was not dependent on the neighbouring end.

In the French system of reeling, the two neighbouring ends twine with each other for agglutination of the filaments. This type of twining is called the chambon type of croissure.

The Italian system of reeling is not found in the silk reeling industry except for some silk reeling areas in the Kolar district of Karnataka state in India. However the French type of reeling is still in vogue in Karnataka and is termed as Charaka reeling.

The direct reeling of the Italian type comprised of a reeling table with stand and basins for water on each table. Each basin was about one metre in width and had 10 threading ends. The frame with glass pulleys to facilitate croissure and guide the thread to the large reels placed at a distance of about 2 mts. The basins were connected with water pipe connections, cold water tanks were fitted to each basin, with ball valves for maintaining a constant level of water in the tank.

**Factors Influencing Silk Reeling**

The following factors play an important role for smooth unwinding of filament from the cocoon and in improving the quality and quantity of raw silk yarn. They are:

1. Reeling bath
2. Jetteboutte
3. Button
4. Croissure
5. Stop motion device
6. Traverse guide
7. Yarn winding speed

**Reeling Bath**

After detecting the correct end of the cocoon filament, the softened cocoons are transferred into a metallic tub called reeling basin on the reeling machine. Luke warm water at a temperature of 33 to 40°C is maintained in the tub and the unwinding of the filaments are done in this water media. Temperature and quality of water play an important role.

The quality of water used in reeling influences the raw silk production and its quality. Generally the pH of reeling water should be between 6.5 and 7.0. Such water converges the sericin molecules on to the filament surface and avoids loss of excessive sericin. Due to the convergence of sericin on to the filament, neatness and cleanness characters of raw silk yarn also improves.

During reeling, water in the reeling basin gets turbid and the concentration of the water is increased due to sericin dissolving into the water and also the acidic matter getting released from the cocoon and
pupal body. High concentration of the reeling water reduces cocoon reelability, thereby affecting the uniformity of the yarn. Further more, the raw silk colour becomes dull, as the turbid matter adheres on to the silk surface. Hence the concentration of the reeling water has to be low and has to be uniformly maintained in all the basins to avoid variations in the colour of raw silk yarn from basin to basin especially during reeling of yellow cocoons. In order to maintain uniform concentration of water, a definite quantity of water has to be supplied to each basin and should have an over flowing facility.

The temperature of reeling water is another important factor which has to be considered for producing good quality raw silk. Higher temperature increases the sericin dissolution into the reeling bath. This increases the reelability of the cocoon, cohesion and smoothness of raw silk, but will reduce the cleanliness of the raw silk, as high dissolution of sericin leads to silk coming off the cocoon surface in lumps. Large lumps of silk are called slubbs or sluggs which cannot pass through the button hole, get obstructed leading to thread break or reel stoppage due to the increase in yarn tension which reduces the reeling efficiency.

If the temperature of the bath is low, the reelability is reduced, which leads to irregular denier of the yarn, reduction in cohesion and increase in silk reeling tension which affects the elastic properties of the raw silk yarn. Generally, it is considered that the reeling bath temperature has to be maintained at 30 to 45°C. For floating system of cocoon reeling, the temperature is slightly higher at 40 to 45°C and in between 30 to 35°C for sunken system of cocoon reeling.

Over-cooked cocoons have to be reeled in a low temperature bath. Cocoons which have poor reelability or cooked in the pan method of boiling have to be reeled in a high temperature bath.

**Jetteboutte**

Jetteboutte is the device which facilitates the new cocoon filament to join the group of filaments being unwound in the event of filament breaks, so that a uniform denier raw silk yarn is produced. In the absence of jetteboutte, the operator has to filing the new filament on to the group of filaments, which is a skilfull operation and requires trained personnel with good eye sight for efficient reeling and to maintain the target yarn denier.

The jetteboutte which can also be termed as end gathering device consists of an inner brass or stainless steel tube and is fixed on to the stainless steel plate above the reeling tray with a lock nut. On this tube is a loosely fitting circular outer casing made of moulded nylon or HDPE and fits over the tube with the help of nylon bushes. The outer casing has a flange at one end for accommodating the driving belt for its rotation and the other (bottom end) is extended into a curved portion like wings or fins as in fig. 1.

Each end derives its rotation by frictional contact from a moving polyurethane endless belt. Generally the speed of the jetteboutte is between 400 to 600 rpm.

When a filament has to be joined to a group of filaments being reeled, to maintain continuity and also uniform denier of the raw silk yarn, the new filament is fed to the revolving fins of the jetteboutte, which pulls up the filament, cuts the end and draws the filament into the tube such that it joins the remaining filaments. By this mechanism, filament feeding is made easier even for an unskilled operator. The end feeding efficiency and the uniformity of the raw silk yarn is improved. Whereas in reeling machines without jettebouttes namely cottage basin, etc. the operator has to fling the filament end on to the group of filaments, which is a highly skilful job. This flinging of the filament end may also result in the extra length of the filament end forming a loop or folding up on the raw silk yarn which is considered a bad cast or loop and is a cleanliness defect of the yarn.

**Button**

This is a circular ceramic device 20 to 25 mm diameter with concave and convex surfaces and a hole of definite size in the center. This device is mounted in a button holder just above the jetteboutte, such that the filament is passed through the hole. The function of the button is to eliminate excess water adhered
onto the silk filaments, combine the loose filaments and obstruct lumps of filaments which may arise due to poor quality cocoons or faulty cooking process, from getting into the raw silk yarn.

The size of the button hole is an important factor in reducing the cleanness defects and also the reeling efficiency. Generally the size of the button is 2 to 3 times more than the average size of the raw silk yarn being reeled. Hence, any waste material three times bigger than the average diameter of the yarn is not allowed to pass through. The average diameter of the button hole is shown in the Table.

If the diameter of the hole is much smaller than its standard size the yarn reeling tension increases, which leads to yarn breakages or reels stopping frequently, reducing the efficiency of reeling. If the whole diameter is much higher, slubbs pass through the hole causing cleanness defects.

Different types of button devices such as the ceramic buttons are available which are cheaper but with a short life. Aluminium alloy buttons even though costly are tamper proof and has a long life. Stainless steel buttons similar to yarn clearing device are also available. However, the ceramic buttons are most common in the industry. The buttons are generally placed with the concave surface being upwards in the Indian silk industry. Fixing the button in this position will lead to water particles collecting in the concave portion and resettling on the filaments. In China the buttons are fixed with the convex surface upwards, such that the water particles slide and drop into the reeling bath. Retaining the size of the hole is important for maintaining the quality of yarn.

**Croissure**

The filaments from the buttons are made to pass over plastic pulleys and coiled with itself or with the neighbouring end. This portion of the filament which is coiled is termed as croissure and the pulleys facilitating the coiling are called croissure pulleys.

The objective of a croissure is to bind the filaments drawn from the button by the coils so that the individual filaments are bound together under the coils pressure to make a compact raw silk yarn. This binding is obtained due to the wet sericin on the filaments which agglutinate or cement the filaments together.

If proper agglutination is not obtained, the filaments get separated easily by the slightest abrasion which arises during the fabric manufacturing process. Such loose binding of filaments show poor tensile properties. Hence, croissure improves the cohesion property of the raw silk yarn.

Further more, croissure squeezes out the water from the raw silk yarn (water adhering on to the filaments as they are unwound from the cocoon in the reeling bath). If the water is not eliminated, the softened sericin on the yarn forms gum spots as it dries on the reel. Croissure also brings circular cross sectional shape of the yarn, by which the lustre of the yarn is increased.

Two types of croissure are generally adopted in the reeling industry to achieve the desired objective. They are (i) Chambon or the French type of croissure and (ii) Tavelletta or the Italian type of croissure.

**Chambon Croissure**

This type of croissure is not commonly adopted in the silk reeling industry except in some of the conventional reeling devices such as the hand operated charaka due to a number of disadvantages.

In this type of croissure, filaments from two neighbouring ends are coiled around each other and the threads are drawn once again to the respective reels for winding the compact yarn.

The passage of yarn during the formation of Chambon croissure is as shown in the fig. 3. As the required tension is low in this croissure, the degree of agglutination of the filaments is low. If any one of the two threads breaks during reeling, the broken thread joins with the unbroken thread and winds on to the reel causing double thread in the hank / skien which is a major raw silk yarn defect.

**Fluidized Beds to Textile Processing**

The technique of fluidization, though known for the last fifty or so, excited industrial interest only recently. It was first introduced in the petroleum industry during World War II. The inherent advantages of
this technique are: (i) exposure of a large specific surface for the reaction; (ii) high thermal conductivity of the reaction surface; (iii) excellent control and uniformity of temperature; and (iv) high overall heat-transfer coefficient. These advantages have made this technique applicable in many commercial operations, such as roasting of gold ores, calcination of limestone, manufacture of carbon black, phthalic anhydride, hydrocarbons and chemical synthesis from hydrogen and carbon monoxide, catalytic dehydration and dehydrochlorination, selective diffusion of gases, etc.; it is also reported to be applicable to the reduction of iron ores and manufacture of cement.

Of late, this technique has attracted the attention of textile technologists as well. For the last three years, the British Rayon Research Association in U.K. and the Shri Ram Institute for Industrial Research in India have taken up the development of this technique for textile processing.

Bed Characteristics

When a fluid is caused to flow upward through a bed of suitably sized solid particles at a velocity sufficiently high to buoy the particles and to impart to them a violently turbulent motion, the bed exhibits characteristics similar to those normally associated with fluids, such as, mobility and hydrostatic pressure, and hence this bed is called Fluid Bed or Fluidized Bed; the technique is known as Fluidization.

The effects of different variables on some of the characteristics of the bed are discussed below:

Velocity of fluidizing medium—The relation between velocity of the upward flow of gases and the pattern of fluidization and also the pressure drop of the upward flow of gases are shown in Fig. 1 & 2.

Fig. 1a represents a vertical pipe containing a fixed bed of solid discrete particles supported on a grid, a steam of gas entering below the grid and passing upward through the bed and two pressure taps P1 and P2 located about the middle of the packed height and at a distance of L. Fig. 2 shows graphically, in the logarithmic scale, the relation between superficial upward gas velocity and \((P1 - P2)/L\). On increasing the velocity of upward flowing gas gradually from zero, the gas passes through the voidage in the bed without any movement of the solid particles; this is represented by curve OA in Fig. 2. On increasing the velocity of gas, there is a slight expansion of the bed and readjustment of particles so that the bed attains the loosest stable configuration (Fig. 1b); this is represented by curve AB. At point B, \((P1 - P2)/L\) has reached a value equal to the weight of solids per unit tube cross-section between the taps P1 and P2. The condition at B is known as dense homogeneous phase or incipient fluidization.

On further increasing the velocity of gas, a part of the gas flows through a denser but expanded bed which constitutes a continuous phase while the balance of the gas passes through the bed in the form of bubbles which constitute a discontinuous phase (Fig. 1c). Now the solids are violently agitated; this condition may be termed as turbulent or two-phase fluidization, which is represented by curve BD. At point D the number and size of bubbles increase and as a result a number of them coalesce and grow to a size equal to that of the tube before escaping from the bed and this creates gas pockets pushing short columns or slugs of solid particles up the tube. Every few seconds a bubble burst through the top of the tube. This is termed as slugging (Fig. 1d).

On increasing the velocity still further, a disperse or dilute homogeneous phase fluidization results (Fig. 1e) which is represented by the curve HF. Point F at which only one particle remains, represents the balancing velocity for a single particle or that of the largest particle in any mixture and falls on the curve OEG which represents the pressure drop for the flow of gas alone through the empty tube.

Heat transfer coefficient—The overall heat transfer coefficient in a fluidized bed is higher than that in a packed bed and far higher (40-100 times) than that in a gas convection system on account of the reasons given below:

The heat transfer coefficient in the fluidization bed is not affected by the thermal conductivity of the solid particles constituting the bed (the thermal conductivity of the bed is about 100 times that of silver). The heat transfer coefficient increases gradually with increase in the mass rate of gas flow till the bed starts
slugging (corresponding to the point D in Fig. 2). On further increase in mass rate of gas flow, there is a steep fall in the heat transfer coefficient (sometimes as much as 50%). The effect of mass rate of gas flow is shown in Fig. 3.

The effects of particle diameter and solid concentration or bulk density of the bed are also shown in Fig. 3. The smaller the particle diameter, the higher is the heat transfer coefficient. With increase in solid concentration, the heat transfer coefficient gradually increases, reaches a maximum and gradually falls down.

Slugging—As the heat transfer coefficient in the fluidized bed is considerably reduced (to the extent of 50%) by slugging conditions in the bed, it is important to consider the effects of different variables on slugging conditions.

The effect of diameter of the solid particles constituting the bed and the ratio of density of the particles to that of the fluidizing medium are shown in Fig. 4, wherein curves DP1 and DP2 represent the bed density versus ratio of particles density to fluid density of the bed of particle sizes DP1 and DP2. At low ratio of particle density / fluid density, \( rs/rf \) (corresponding to \( P \)), the bed of particle size DP1 will fluidize without slugging, while the bed of particle size DP2 will slug between bed voidages of A and A¢, while the bed of particle size DP1, will fluidize with slugging at \( rs/rf \) represented by \( Q \) between bed voidages B and B¢.

The effect of increasing the height/diameter ratio of the bed is similar to that of increasing the diameter of particles constituting the bed. The higher this ratio the wider is the range of bed voidage during which slugging occurs, and the lower is the heat transfer coefficient.

It has been found that the dimensionless group \( Dp \times Lf/A \) or \( (\text{particle diam.} \times \text{bed height})/(\text{cross-sectional area of bed}) \) defines the transition from the flow (Type 2) in the ordinary fluidized bed to that (Type 1) in the slugging bed, the transition value being 0.008. In Fig. 5, Type 1 curve corresponds to \( DpLf/A > 0.008 \), where the heat transfer coefficient decreases as the height increases; and Type 2 curve corresponds to \( DpLf/A < 0.008 \), where the heat transfer coefficient increases to a maximum and then falls down with increase in bed height. From the relationship \( DpLf/A \) it is clear that the higher the ratio of height to cross-section of the bed and greater the particle diameter, the greater is the slugging tendency.

Reaction of Cellulose with Crosslinking Agents

Cellulose consists of long chains of glucopyranose residues linked through 1:4 \( \beta \)-glucosidic bonds. These chains are close packed with some degree of order in the so-called crystalline regions, whereas in non-crystalline regions, the glucopyranose residues are present in a more or less disoriented arrangement. Along the \( b \)-axis, the chains are held together, forming a sort of laminae or micelles, by hydrogen bonds, which are most likely to be formed in the more orderly crystalline regions. Along the \( c \)-axis there are only weak Van der Waals forces between the laminae.

A certain degree of confusion exists in the use of the terms ‘amorphous’, ‘crystalline’, ‘accessible’ and ‘inaccessible’ regions, and values obtained for these by different authors vary according to the methods used for their measurement. There is also some confusion in the notations for the axes. Whereas crystallographers call the fibre axis or the axis along the length of the molecular chains as \( b \)-axis, physicists and chemists call this the \( a \)-axis. In spite of all this, cellulose can be described as a three-dimensional polymer, in which there are strong covalent \( \beta \)-glucosidic bonds along the \( a \)-axis, hydrogen bonds along the \( a \)-axis, hydrogen bonds along the \( b \)-axis and weak Van der Waals forces along the \( c \)-axis, and in which the long chains of glucose anhydride units are arranged in different degrees of order and disorder in different portions of the macromolecule. Cotton and viscose both have the same basic structure; they differ, however, mainly in their average degree of polymerization and the amount of amorphous or accessible region. Thus while cotton has a
degree of polymerization (D.P.) of c. 3,000 with 15 to 30 percent accessible region, viscose has a D.P. of 400-500 and has 50 to 60 percent of accessible region.

The two main weaknesses of cellulosic textiles, namely, poor dimensional stability in wet treatments and ease of creasing, can be understood on the basis of the structure of cellulose. When cellulose is treated with water or other aqueous solution, they enter into the accessible region and produce cross-sectional swelling by overcoming the weak hydrogen bonds and Vander Walls forces along the b- and c-axis. It can be easily seen that such a swelling of fibres in a yarn would result in longitudinal shrinkage due to constraints placed on the fibres by the yarn twist. Similarly, cross-sectional swelling of yarn in a fabric results in a shrinkage along the length and width.

When a tensile stress is increasingly applied to a cellulosic fibre, the weak hydrogen bonds between molecular chains are easily broken producing slippage of one chain against another till the fibre ruptures. Thus, in the stress-strain behaviour of these fibres, there is, at relatively low strains, a large area of plastic flow or time-dependent creep, where the extension produced is non-recoverable. This poor elastic performance is responsible for the easy creasing of cotton and rayon fabrics.

In order to reduce water-imbibition and improve crease recovery, attempts have been made to introduce covalent cross bonds between glucose residues on neighbouring chains of the cellulose molecule. Since the early attempts of Eschalier\(^1\) and, a little later, of Cross and Bevan\(^2\), to improve the wet strength of rayon by treatment with formaldehyde and acetic or lactic acid, followed by drying at 40-50°C., considerable progress has been made, and many reagents have been used to cross link cellulose. However, it is only in recent years that we have obtained some understanding of the mechanism of simple cross linking reactions, such as that of cellulose with formaldehyde. It would not be out of place to review, in some detail, the significant results reported in this field.

Meunier and Guyot postulated that methylene bridge, -O-CH2-O-, are formed by formaldehyde with two glucose residues of cellulose. Wood disagreed with this postulate and suggested that methylene bridges were formed on two hydroxyls of the same glucose residue or, alternatively, that hydroxy-methyl groups, R-O-CH2-OH, were formed in the hydroxyls of cellulose. According to Schenk, the changes brought about by formaldehyde in the properties of cellulose can be explained by the formation of cross links between two adjacent cellulose molecular chains. Dilleniusb also arrived at the same conclusion from a review of earlier work.

Reaction 5 is not very likely to occur, since it involves the formation of a 3-membered ring. Reactions 1 and 3 involve the formation of hydroxy-methyl groups without any loss of water. Reactions 2 and 4, on the other hand, lead to the formation of ethers with removal of one molecule of water and give products which are stable to hydrolysis. In reaction 6 also, there is no loss of water. Again, the combining weight of formaldehyde will be 30 in reaction 1 and multiples of 30 in reaction 3, depending on the value of \(n\). On the other hand, the combining weight of formaldehyde in reaction 2 is only 12, whereas in reaction 4, it is 21, 24 and 25.2 respectively, for \(n = 2, 3\) and 4.

Gruntfest and Gagliardi used experimental data on material balance, amount of fixed formaldehyde and combining weight of formaldehyde to study the mode of reaction.

When rayon was treated with 20 per cent formaldehyde and different concentrations of hydrochloric acid catalyst, approximately equal weight gains were obtained after curing. However, on boiling with water, there was a loss in weight of products cured with higher acid concentrations. Similar results were obtained by using catalysts of widely varying acidities. This suggests that there is a substantial change in the nature of the product of cellulose-formaldehyde reaction as the acidity of the catalyst increases. It is likely that under alkaline or weakly acid conditions of curing, reactions 1, 3 and 6 take place. Under strongly acidic conditions of curing, reactions 2 and 4 are more probable.

The combining weight of formaldehyde varies with its concentration in cellulose. At lower
concentrations, the combining weight approaches a value of 12, corresponding to the formation of simple methylene ethers as in reaction 2. At higher concentrations, the combining weight increases and ethers of the type $Z-O(CH_2O)_n-Z$ are probably formed according to reaction 4. Reduced eater-imbibition, insolubility in cellulose solvents and increased fibre stiffness and elastic recovery also point to the formation of cross links.

Wagner and Pacsu used a different approach in the study of the cellulose formaldehyde reaction. They argued that if some of the hydroxyls of cellulose were involved in cross link formation, this should be reflected in the results of methylation and methanolysis of the methylated product and in such reactions as periodate oxidation. By reacting acid-treated cotton with formaldehyde in the vapour phase at 110-150°C for 1-24 hr., they obtained a fixed formaldehyde content of 5 percent or more. Methylation of the product gave a methoyl content of c. 32 per cent against 43 per cent methoxyl for untreated native cellulose. If each molecule of formaldehyde reacts with two, and only two, hydroxyls in cellulose and complete methylation of all residual free hydroxyls was obtained, the theoretical methoxyl content of the product should have been 37.2 per cent. This was a definite evidence that the reaction occurred between monomeric formaldehyde and two cellulose hydroxyl groups, and that the fixed formaldehyde was covalently bonded to the cellulose molecule.

Methanolysis of methylated formaldehyde-reacted cellulose gave 39.1 per cent of 2, 3, 6-trimethyl glucoside, 31.9 per cent dimethyl methyl glucoside and 29.0 per cent monomethyl methyl glucoside. The dimethyl derivative represents the fraction of glucose residues in which one hydroxyl is involved in a methylene bridge, while the monomethyl derivative represents those glucose residues in which one hydroxyl is involved in a methylene bridge and the bridge inhibits the methylation of an adjacent hydroxyl. The yield of trimethyl methyl glucoside agrees well with the assumption that each molecule of formaldehyde substitutes two, and only two, hydroxyl groups. The complete absence of 2, 3-dimethyl methyl glucoside shows that the primary hydroxyl groups are not involved in methylene bridges. This was further confirmed by the results of periodate oxidation; periodic acid consumption was much lower for formaldehyde treated cellulose than for natural cellulose.

Karrholm studied the changes in bending, torsion and stretching moduli as the amount of formaldehyde (both fixed and soluble) in viscose rayon was increased. It was observed that all three moduli increased with increase of formaldehyde, passed through a maximum at 5-7 per cent formaldehyde content, and then decreased (Figs. 1 and 2). If one molecule of formaldehyde reacts with two hydroxyl groups in different glucose units, the maximum amount of formaldehyde in the fibre would be:

$$= 9.3\%$$

If the reaction is confined to the amorphous parts only, the maximum would be approximately $9.3 \times 0.6 = 5.6$ per cent. If was concluded that as the concentration of formaldehyde is increased, an increasing number of short cross links is formed giving an increase in the moduli up to c. 5 per cent fixed formaldehyde. When the fixed formaldehyde is 7 per cent, some of the cross links are longer, consisting of two or more formaldehyde molecules, producing a decrease in the moduli. The moduli decreases further as the fixed formaldehyde increases to c. 9 per cent, when most of the cross links probably contain on an average two formaldehyde molecules.

Formaldehyde treatment confers dimensional stability, crease-resistance and reduced water-imbibition to cotton and rayon materials. However, the acid catalysed reaction also causes cellulose degradation and brittleness. Various alternative methods have been tried to produce cross bonding; some of them are mentioned here. Glyoxal reacts readily with viscose in the presence of an acid catalyst. The reaction is analogous to that with formaldehyde and the probable cross bonds formed are:

- Borax also forms cross bonds with viscose cellulose. The bonds are, however, different in that coordination complexes, not covalent links, are formed.
The energy of this bond is 10–20 kg. cal. as compared to 80–100 kg. cal. for a covalent bond. The bond is broken by water and by chemical treatment. Derivatives of ethylene urea, produced by the interaction of ethyleneimine and an isocyanate, are also capable of producing cross bonds. The reaction occurs at comparatively low temperatures (100–120°C.) without a catalyst, according to the following mechanism:

Dimethyloformamide also forms cross bonds with viscose in the presence of an acid catalyst. The reaction is as follows:

Dimethyloformamide liberates formaldehyde and forms ether links, its residue being attached to the cellulose at the end of the reaction to give the formamido-methyl ether.

**Nitrocellulose**

Nitrocellulose, a misnomer for cellulose nitrate, is an important commercial product. It is an essential ingredient of blasting explosives, and a base for propellants. It is also used in the celluloid and lacquer industries.

Braconnot in 1832 observed the formation of inflammable materials by the action of nitric acid on cotton, starch and wood fibre, and obtained impure products which he called xyloidines. Pelouze in 1838 investigated the action of nitric acid on cotton. The technological importance of the process was recognized in 1846 by Shonbein who took out a patent for nitrated cellulose obtained by treating cotton with a mixture of nitric and sulphuric acids. The products obtained by him were, however, unstable and there were some serious explosions, the worst being the one in Faversham in 1847. This led the governments in several countries to ban its manufacture and use.

Subsequent progress was in the direction of preparing a stable product and the classical researches of Abel led to the understanding of the cause of instability, and to the manufacture of stable nitrocellulose.

The three alcoholic groups—two secondary and one primary—present in each glucose residue of the cellulose chain may react giving three or more compounds corresponding to the successive nitration of the three hydroxyls. The final product of the reaction should be trinitrate C6H7O5(NO2)3 with a nitrogen content of 14.15 per cent, but it is not possible to obtain a stable product with this nitrogen content by the action of sulphuric and nitric acid mixtures. By using special techniques, it is possible to obtain a product nearing this theoretical composition. However, in actual practice, a series of substances with nitrogen contents varying from 10–13.5 per cent are prepared. The various grades of nitrocellulose usually met with in industry, and their uses are given in Table 1.

Nitrocellulose was first prepared in India at the Cordite Factory, Aruvankadu, which is even today the only factory producing it. Till very recently, the only use of nitrocellulose was for defence purposes. During the last three years, the Factory has been supplying nitrocellulose of grade (iii) to manufacturers of artificial leather, book binding cloth and lacquers, and so far 170 tons of this material has been supplied. It has been estimated that the paint industry will require 500 tons of nitrocellulose per annum during the second Plan period. The gelignite industry, sponsored by the Government of India, in collaboration with Messrs Imperial Chemical Industries, also uses nitrocellulose. Proposals for the manufacture of raw photographic films in India are also under consideration. Thus the demand for nitrocellulose is continuously rising.

The raw materials in common use are cotton, in the form of spinners’ waste or linters, and paper. Where cotton is plentiful, linters constituted the cheapest raw material, as they are otherwise wasted and their removal is essential both for oil recovery from cotton seed and for utilizing the oilcake as cattle feed. Process of production

Hard spinners’ waste, available from textile mills, is used as the raw material at Aruvankadu. This material is expensive, as it finds other uses and has also a good export market. In England, paper in the form of scrolls or sheets, cut into small pieces, are used for nitration.
Cotton waste is first treated to remove waxes, lignin, hemicellulose, etc., by boiling with alkali pressure, a process called ‘kiering’. The kiered product is washed free of alkali and dried. The process of kiering, washing and drying has to be done under properly controlled conditions as otherwise the product tends to ball up or form knots and the penetration of acids, in the subsequent treatment is hindered. The displacement process (Fig. 1) is largely employed for the nitration of the cleaned material. The process consists in dipping the cotton in mixed acid for hr. at the end of which the acid is slowly displaced by water.

The nitrated fibre is boiled in lead-lined vats a number of times, with changes of water between boils. The initial acidity which is c. 0.10 per cent goes down to 0.04 per cent. In Aruvankadu (height above sea level, 6,000 ft.) normally two boils of 8 hr. duration at a pressure of 7 lb./sq. in., corresponding to a temperature at 105°C. are done.
The stabilized material is beatered in hollenders, of the type used in paper industry, in a faintly alkaline medium. It is subjected to a series of washes, called potchering, to remove impurities. Finally, as nitrocellulose is liable to slow decomposition even at ordinary temperatures of storage, a small quantity of finely divided precipitated chalk is added to the material to neutralize any acid that may be produced during storage. The material is then centrifuged and sold either ‘alcohol-wet’ or ‘water-wet’. For some special uses, diphenylamine (1%) is used as stabilizer.

Nitrated cellulose retains most of the physical characteristics of the original raw material, except that the fibres are hard and brittle.

**Effect of Varying Nitration Conditions**

Despite the wide range of permissible variations in the proportions of nitric acid, sulphuric acid and water in industrial practice, the selection is limited by considerations of cost and also of the marked swelling or dissolving action on the fibre exhibited by some of the compositions. Using cotton waste as raw material and the displacement process for nitration, a mixed acid containing sulphuric and nitric acids in the ratio of 1 : 3, gives a nitrocellulose containing 13 per cent nitrogen; with a mixed acid containing sulphuric acid, 62.5; nitric acid, 22.5; and water 15 per cent, a product containing 12.2 per cent nitrogen is obtained. Further, while the production with the first mixture is soluble in ether-alcohol (2:1) to the extent of only 10 per cent, the latter is completely soluble in the mixed solvent. This difference in solubility is one of the criteria for distinguishing guncotton from other types of nitrocellulose.

Nitration conditions have a significant bearing on the viscosity of the resultant products, a property of extreme significance in its use for particular purposes. It has been shown that by substituting anhydrous phosphoric acid or by using phosphorus pentoxide and nitric acid at 0°C., a very high degree of nitration is obtained, without significant degradation of cellulose. This method has been employed for estimating the degree of polymerization and molecular size of the original cellulose.

The main characteristics of nitrocellulose are its nitrogen content and viscosity. The latter depends on the raw material employed and the condition of nitration. The viscosity can be brought down to any limit, either by degrading the raw material before nitration or by depolymerizing the nitrated material by boiling under pressure. The latter is the preferred method, as the preliminary degradation of raw cellulose results in a friable material difficult to handle and entails heavy losses in processing. During pressure boiling, a certain amount of acidity develops by hydrolysis and some nitrogen is lost. By suitable control of pressure and time, any required type of product can be produced. In some cases, as in the case of low-viscosity industrial nitrocellulose, pressure boiling achieves both stability and degradation.

In trade practice, ether-alcohol solubility provides the criterion for the grade of nitrocellulose. This solvent is scarcely suitable for viscosity determination. Acetone can also be used, but it is hygroscopic. The Imperial Chemical Industries use a mixture of 95 per cent acetone and 5 per cent water as solvent. Butyl acetate and ethyl acetate have also been used, but here again the purity of the solvent is important in viscosity determinations. In American practice, the solvent in use (Hercules solvent) consists of mixture of 20 parts ethyl acetate, 25 parts alcohol and 55 parts toluol by weight, and viscosity determinations are made with a 1 per cent solution for highly viscous types and a 12.2 per cent solution for degraded material.

The molecular weight of nitrocellulose is determined by osmometric method. However, true values obtained by the method are different from those obtained by viscosity methods.

**Dissolving Pulp for Rayon Industry**

Dissolving pulp, a highly purified form of chemical pulp, is the chief raw material employed in the manufacture of rayon, cellulose acetate, cellophane, nitrocellulose, methyl cellulose, ethyl cellulose and other cellulose derivatives.

To meet the requirements of industry, which produces 47 tons of rayon per day. India at present
imports dissolving pulp values at Rs. 1.8 crores per annum. If we are able to utilize indigenous cellullosic raw materials and establish a dissolving pulp industry in India we will be able to effect a saving in foreign exchange to the tune of Rs. 6.5 crores per annum.

**Viscose Rayon Manufacture**

In the manufacture of viscose rayon (Fig. 1 & Table 1 and Fig. 2), dissolving pulp, usually bleached sulphite pulp, is steeped in sodium hydroxide solution of 18 per cent strength at 20°C. for 1 hr. to form soda cellulose. The steeped pulp is then pressed to yield alkali cellulose which contains: cellulose, 30; sodium hydroxide, 15; and water 55 per cent. The pressed out alkali is generally reused after recovery. The pressed alkali cellulose is shredded at 23°C. for 1 hr. and aged in the presence of air at a temperature of 20°C. for c. 30 hr. Ageing is essentially a cellulose depolymerization step and is optimized to yield a product of the desired viscosity for later operations.

The aged alkali cellulose is then reacted with carbon disulphide at 28°C for hr. to form sodium cellulose xanthate. The xanthated mass is dissolved in dilute caustic solution at 18°C. in the course of hr., to give colloidal 'viscose' containing: cellulose, 7.5; sodium hydroxide, 6.4; and total sulphur, 2.2 per cent. It is then filtered to remove unreacted cellulose fibres, foreign impurities and gels, deaerated under vacuum and ripened and 20°C. for c. 40 hr. Cellulose xanthate partially de-esterifies during ripening, and many side reactions also occur.

Ripened viscose is pumped through spinnerettes into an acid spinning bath to give a continuous filament. During spinning, the excess of caustic is neutralized, xanthate is de-esterified and regenerated cellulose molecules are oriented by the spinning stretch. The spun yarn in the cake is then washed, desulphurized, bleached, finished, dried, conditioned and rewound in the form of cones or hanks.

**Dissolving Pulp Specifications**

In the selection of dissolving pulp, two major considerations are involved, namely: (i) commercial, e.g., price and availability, and (ii) technical e.g., case with which the pulp responds to rayon making and the effect of pulp constituents on the yield and quality of the final product. This paper deals mainly with the technical aspects of pulp selection.

Dissolving pulp is generally prepared from wood and as such, it contains wood constituents, the proportions of which depend upon the extent of pulping. The results of pulp analysis (Table 2) indicate that pulp contains alpha-, beta-, and gamma-cellulose extractibles, ash components and small proportions of other constituents.

Alpha-cellulose has been arbitrarily defined as the fraction which remains insoluble when pulp is treated with 17.5 per cent sodium hydroxide, at 20°C. for 30 min. It corresponds to cellulose with a degree of polymerization (D.P.) exceeding 200. Viscose rayon has a D.P. range of 250 to 350 and the alpha-cellulose value gives a measure of the overall pulp yield and quality. Pulp consumers are interested in getting a pulp containing high alpha-cellulose. The determination of alpha-cellulose, however, provides no information on the polymolecularity of long chain molecules and this necessitates the measurement of D.P.

Hemicellulose is the term applied to polyoses, mainly xylans, arabinans, glucosans, galactans, mannans, etc., which are removable by cold or hot dilute alkali. As they are present in relatively small quantities in dissolving pulp, rayon manufacturers evaluate hemicellulose in terms of Cross and Bevan’s beta- and gamma-cellulose.

A certain amount of hemicellulose is necessary in paper pulp in order to impart a high degree of hydration, but for dissolving pulp, except for that required for sheet formation and its swelling, hemicellulose is usually an undesirable constituent. Cellulose molecules of less than 200 D.P. are usually incapable of producing a coherent fibre. It is still uncertain whether the chemical configuration of hemicellulose influences pulp quality; the degree of polymerization and its physical state are far more important than chemical constitution.
Beta-cellulose is that fraction which gets precipitated when soluble pulp extractibles, obtained by treating pulp with 17.5 per cent sodium hydroxide at 20°C. for 30 min., are neutralized. This fraction includes polyoses with D.P. ranging from 10 to 150.

Gamma-cellulose is that fraction which remains in solution when the soluble extractibles obtained by treating pulp with 17.5 per cent sodium hydroxide at 20°C. for 30 min. are neutralized. This fraction includes polyoses with D.P. up to 10.

Low molecular fractions of cellulose that remain unextracted during steeping undergo xanthation and appear in the yarn. They do not contribute to yarn tenacity and they, therefore, act as diluents or fillers. Moreover, the solubility of cellulose xanthate is influenced by the chain length of cellulose; the smaller the chain length, the greater the solubility of the xanthate found. Soluble xanthates hinder the effects of spinning stretch. It is desirable, therefore, to keep the concentration of low molecular fractions to a minimum.

**Degree of polymerization:** The effect of chain length distribution on the properties of rayon has been extensively studied. The changes in the D.P. of cellulose during viscose rayon manufacture are given in Fig. 3. A rayon pulp of good quality should be as uniform as possible with respect to molecular size, and the purpose of ageing in viscose manufacture is to make the chains uniform with respect to D.P.

Cellulose degradation to a D.P. of c. 500, as brought about by the oxidation of alkali cellulose, removes the differences in molecular weight distribution in pulps. It appears, therefore, that molecular weight distribution is not an important characteristic of viscose pulps which are subjected to alkaline ageing.

The yarn tenacity increases with the increase in D.P. up to 350–400 after which the relationship is asymptotic. Published word in this field indicates the desirability of keeping the D.P. of finished yarn in the range of 375–450 (Fig. 4).

**Copper number:** The reducing power of cellulose is usually expressed in copper number, which represents the copper in Fehling’s solution reduced by 100 g of cellulose. The copper number of cotton cellulose ranges from 0.05–0.08; higher copper numbers indicate degradation. Bleached sulphite wood pulps have a copper numbers of 1.5–2.5 and as it provides chiefly a measure of hydrocellulose and oxycellulose in the pulp and gives no additional information to that given by alkali solubility and viscosity tests, copper number is seldom determined.

The non-cellulosic constituents of pulp have a pronounced effect on processibility. They should be as low as possible without affecting the uniformity of the pulp.

**Ash constituents:** Alkaline earths, such as calcium and magnesium, hinder pulp reactivity and result in poor viscose filtration. High percentage of silica also has a similar effect. Calcium is detrimental also because it tends to cause incrustations around spinnerette holes.

The rate of alkali cellulose ageing is distinctly influenced by the presence of certain metals, such as iron, nickel, cobalt, cerium, vanadium, chromium and manganese, which catalyse the ageing process. Nickel has the lowest, and chromium and manganese the highest catalytic effect.

As little as 0.1 per cent iron in wood pulp reduces the ageing time of alkali cellulose to one-fourth the normal ageing time. Even smaller concentrations of iron (0.0018–0.015%) has an appreciable effect on cellulose depolymerization. The presence of copper in small amounts has no effect.

The concentration of lignin, a polymer of phenyl propane groups, should be as low as possible in pulp. Its presence interferes with pulp reactivity.

Ether extractibles: Pulp constituents soluble in organic solvents, like ethyl ether, are fats, fatty acids, resins, waxes and non-volatile hydrocarbons. In small quantities, they act as wetting and emulsifying agents and are, therefore, useful.

Pulp processibility is usually measured by converting the pulp to xanthate and determining the case with which the xanthate dissolves in caustic as measured by the filtration characteristics of viscose.
Filtration is influenced by the processing conditions adopted for viscose manufacture, filter area, filter media and the pressure drop maintained during filtration. The filtration test can be conveniently used to predict pulp processibility by comparing the plot of $d \ln q$ vs. $1/v$ ($v =$ volume of viscose filtered, $q =$ time in min) for a pressure drop of 20 lb./sq. in. using the same filter media and viscose processing conditions as that used in commercial manufacture. A laboratory scale set-up with a filter area of 12 sq.cm. will suffice for the test.

**Pulp uniformity:** Dissolving pulp should be uniform in quality throughout the consignment and also from consignment to consignment. Slight differences in viscosity, xanthate solubility, ash constituents, etc., can have pronounced effect on processing conditions. For stable operation, it is essential that the variations should be very small.

Sutermeister recommends that the viscosity may be considered uniform if viscose made from ten 60 lb. Samples of successive lots of pulp does not vary by more than 6 per cent from the average. Pulp uniformity can also be judged by the alpha-cellulose content of pulp which should not vary by more than ±1 per cent from the average.

The pulp should also show uniformly high solubility as gauged by the filtration characteristics of viscose made from successive lots.

**Geometry of pulp sheets:** Steeping is an important processing requirement as far as sheet information is concerned. A pulp which does not steep well is likely to cause difficulty in the subsequent operations of ageing, xanthation, filtration and spinning. Even under the best commercial conditions, the geometry of books, that is, sheet size, spacing, etc., results in a gradient in alkali content from outside sheets to the central sheet. To avoid this, the pulp sheet should be designed to absorb alkali evenly. The absorption properties of the fibre mass must be balanced against the physical design of pulp sheet. With a correct match between absorption rate and rate of caustic rise due to capillary action, the steeped sheet should neither float nor slump in the press, and it should be free from areas of incomplete penetration. The importance of pulp qualities which affect steeping cannot be over-emphasized, because there are no known ways of adjusting the subsequent processing stages to compensate for the damage suffered from non-uniform steeping.

The effect of different constituents of pulp on the manufacture of rayon have been studied by a number of investigators in Europe, U.S.A., Canada and Japan. Based on their results our own experience in this field, we have arrived at the following specifications for dissolving pulp (Table 3).

As it is not possible to get an exact idea of the quality of rayon which is produced from given pulp specification, complete evaluation of pulp by pilot plant tests is necessary.

### Anti-Crease and Anti-Shrink Finishes for Viscous Rayons

Viscose rayon, a regenerated cellulose fibre, is significantly different from the natural cellulose fibre, cotton. The former has a low degree of polymerization (D.P., 250–600), compared to cotton (D.P., 3,000 and above); it is highly amorphous, the crystallinity being 25-40 per cent as compared to 70-80 in cotton. The characters which viscose rayon possesses owing to these properties are: (i) greater susceptibility to dimensional changes when washed; (ii) low wet strength; and (iii) low tensile strength per unit cross-section compared to cotton.

Apart from molecular configuration, the strains introduced during spinning and weaving, and the strain introduced in rayon fabric during the various stages of dyeing and finishing, have a marked effect on the dimensional behaviour of the fabric. The combined effect leads to a shrinkage of 20-25 per cent in georgettes and a shrinkage of 7-15 per cent in satins, crepes, staple fibre fabrics, etc.
Attempts have been made from time to time to improve the properties of viscose rayon by suitable chemical modification. The earliest attempt by Eschalier is noteworthy. The process proposed by him involved the use of formaldehyde in the presence of acidic catalysts, and it was claimed that shrink resistance and tensile properties of rayon improved as a result of the treatment. The process did not, however, attain commercial success. Interest in the aldehyde treatment of textiles was revived after the end of the First World War Marsh et al. (Tootal Broadhirst & Lea Co.) made a notable contribution when they introduced the urea-formaldehyde anti-crease process. Since then, a number of firms in U.S.A., U.K., Germany, Holland, Japan, etc. have made notable contributions in this field. The main lines of work are:

(i) Treatment with synthetic resin pre-condensates formed from ureamaleneine or their derivatives and formaldehyde; (ii) treatment with aldehydes alone, such as formaldehyde, glyoxal, etc., and (iii) treatment with other cross bonding agents such as vinyl sulphone, epichlorhydrin, potassium disulphate, ethylamine, etc.

Later attempts were in the direction of modifying either the properties of resins or those of cross linking agents in such a manner that there is an improvement in one or more of the following aspects: (i) reduction in brittleness resulting in softer handle; (ii) reduction in chlorine retention resulting in better bleachability; (iii) improvement in wet tensile and wear values; and (iv) improvement in process details, such as type of catalyst, protective agents, and temperature or manner of curing.

India manufactures c. 500 million yards of rayon cloth. A large part of it is processed neither for anti-creasing nor for anti-shrinking (stabilizing). There is an increasing demand for Indian rayon fabrics, particularly in middle and south East Asia. Processing of fabrics for anti-creasing and anti-shrinking will improve the quality of products and stimulate foreign demand.

The Shri Ram Institute took up studies on anti-crease and anti-shrink finishes in 1953. Available techniques were first examined, and later, a new compound, designated Srifirset, which could be used for improving the anti-crease and anti-shrink properties of rayon fabrics was discovered.

**Resin Finishes and Formaldehyde Treatment**

Methods for the preparation of urea-formaldehyde pre-condensate and for treating rayon goods were worked out. The stability of the treating solution was studied at different temperatures and the ‘know-how’ of the process was developed with the object of rendering help to those interested in the process.

The process which uses resins and the process which uses formaldehyde alone, involve three steps:

(i) Padding with treating solution, (ii) drying, and (iii) curing at high temperature.

Attempts were made to simplify the process to eliminate the need for curing. On analyzing the normal formalizing process, it was found that free water present in the treating solution made high temperature curing imperative. A process was evolved in which the free water was bound by the addition of hydrophilic compounds, such as calcium chloride, magnesium chloride and aluminium sulphate. The new process consists in simply treating rayon textiles with a solution containing formaldehyde, acid catalyst and a hydrophilic agent, say calcium chloride, for a certain duration at room temperature, washing and then drying. No baking is necessary. All forms of textile material, viz., fibres, yarns and fabrics, can be treated, and treated fabrics possess better draping qualities and crease recovery; they are also shrink-proof.

As the process appeared attractive a detailed study was undertaken. The effect of different variables, such as duration of impregnation and concentration of acid in the treating bath, were studied. The results are given in Tables 1 and 2.

By increasing the duration of impregnation or the concentration of acid in the treating bath, the shrinkage is reduced and the loss in tensile strength is increased. The result was confirmed by experiments carried out with woven fabric in place of yarn (Table 3). As the loss in tensile strength is high, the process has no practical utility.

**Srifirset Process**
The normal urea-formaldehyde process suffers from the following disadvantages: (i) unstability of treating bath, (ii) many steps, such as padding, drying and curing, involved in the treatment, and (iii) embrittlement of treated fabrics. Attempts made to overcome these defects, resulted in the discovery of a compound, Srifirset (a carbohydrate derivative of urea) and the development of a process for utilizing Srifirset with formaldehyde.

**Development**

The development work involved a detailed study of Srifirset: formaldehyde ratio in the bath. Srifirset concentration, pH of the bath, temperature of treatment and duration of drying. The results are summarized in Tables 4–9.

It has been observed that when the pH of the treating bath is lowered, the shrinkage is reduced. The combined Srifirset increases as the temperature and duration of drying increases; but long exposure at high temperature results of yellowing with loss of tensile strength. The higher the temperature of drying, the lower is the shrinkage. Among the catalysis tried, a mixture of sulphuric acid and aluminium sulphate appears to be the best from the point of view of dimensional stability and minimum loss in tensile strength; ammonium chloride is the best from the point of view of anit-crease properties. It will be seen from the results set out in Tables 4–9 that the optimum conditions for the treatment are approximately as follows: Srifirset-formaldehyde ratio, 1:7; Srifirset conc., 12 per cent for crepes and 8 per cent for georgettes; pH, 2.5; drying temp., 90–140°C; and duration of drying, 1–10 min.

**Heat Treatment of Resin-Treated Cellulosic Textiles**

It is common experience in mills that lack of consistent drying of textiles leads to non-uniformity of the finished goods. This is particularly so in the resin finishing of textiles. Though the technology of resin finishing has advanced considerably, and the known-how of the process involved is well understood, yet the quality of the finished product depends on the experience and judgement of the finisher, in regard to control of conditions, particularly at the drying and baking stage.

The following are the difficulties that finishers encounter in the operations: (i) Non-uniform resin distribution due to non-uniform padding, non-uniform drying, baking and migration of resin; (ii) excessive losses in the physical and mechanical properties of treated material due to surface deposition of resin, excessive drying and/or baking, improper pH control and choice of catalyst; (iii) poor wash-fastness of treated materials due to surface resin, incomplete baking and poor catalyst action; (iv) variation in fabric geometry which affects the degree of drying and baking required and the amount of resin to be applied; and (v) satisfactory handle and feel, which are entirely personal factors and but which nevertheless depend on the factors mentioned above.

The moisture content of the material is an important factor to be taken into consideration during the various stages of operation, particularly drying and baking; moisture content is responsible for (i) the migration of resin, (ii) obtaining the requisite degree and rate of drying and baking, (iii) catalyst activity and pH control and (iv) physical and chemical modification of fibre material.

**Fibre Properties and Moisture Content**

It is well known that moisture plays an important part in modifying the physical and chemical properties of textile materials, particularly cellulosic materials, which contain a large number of hydrophillic groups. Increase in the wet tensile strength of cotton and decrease of the same in rayons may be cited as outstanding examples.

Sorption of water by cellulose is due to absorption and capillary condensation. It is the rigidly held water through strong hydrogen bonding forces which causes hysteresis phenomena; the bonds between cellulose OH groups are broken by water and are not necessarily reformed in the same fashion, thus enabling some water to be entrapped into the structure of the polymer.
It is known that cellulose can contain non-freezable water. These and related phenomena are bound to influence the course of resin polymerization and subsequent physical properties of the treated fibre. For example, it would be interesting to see how far the trapped moisture would help to compensate for losses in tensile strength due to stresses produced by the polymerized resin embedded in the structure; the trapped moisture may help to plasticize the rigid structure of cellulose after resin treatment so that the crystallites could still be maintained in a mobile condition to impart strength to the fibre.

**Modification of Fibre Properties During Heat Treatment**

Preston et al. have shown that thermal treatment of cellulosic fibre leads to distinct modifications depending on the moisture content of fibres. The properties affected are swelling and sorption capacity which decrease to the extent of 50 per cent in cellulose, 30 per cent in silk; the density increases and these results in increased crystallinity up to 4 per cent in cellulose. At the optimum moisture content, the properties are modified to the maximum during the initial stages of heat treatment. With increase in temperature the modifications are more pronounced; after a certain limiting temperature, the tendering of fibre starts. This limit depends on the nature of the fibre but is between 110 and 130°C.

**Temperature and Moisture Content**

When a wet textile fabric is subjected to heat treatment, drying proceeds at a constant rate till moisture content attains a certain critical value, known as the critical moisture content. After this, the rate of drying falls off and there is a rapid rise in the temperature of the fabric depending on the temperature of the source of heat. Therefore, during the period of steady rate of drying, the temperature of the fabric would be the same as the temperature of evaporation of water and thus there would be no risk of excessive temperature being produced on the material before the critical moisture content is reached. This critical moisture content is a specific property of the fibre, and the moisture (per cent) for various fabrics are the following: Cotton, 25; viscose rayon, 28; silk, 27; and wool, 39.

**Tone and Shade Control in Textiles**

“Dyeing is an old industry and development in it for a long time came only slowly; until in fact Perkin synthesized Mauve . . . . It was really the advent of new (synthetic) fibres which demonstrated the need for new dyeing techniques. It was only when grave difficulties were experienced in dyeing a new fibre with established dyestuffs and techniques, that new techniques were evolved . . . . New dyeing processes were, therefore, forthcoming to meet the special demands of new fibres, but when once the new processes had been developed, their use was extended to natural fibres too and often with beneficial results.” These new dyeing processes envisage continuous operation at elevated temperatures.

Steps in continuous dyeing—Continuous dyeing of textiles consists of the following steps: (i) Passage of the fabric through the dye solution or dispersion (liquid treatment); (ii) padding to obtain uniform distribution; and (iii) heat treatment to obtain diffusion and fixation or chemical reaction of the dye molecules with the fibre substance at localized sites in a short time.

Each of these steps is a technique by itself requiring efficient control, since it is difficult to rectify the mistakes at the subsequent step. Hence it is needless to stress the importance of the factors that are responsible for the efficiency of each of these steps in obtaining well-penetrated, uniform solid shades without any adverse effect on the tone of dyeing.

Liquid treatment—The passage of cloth through the dye solution or dispersion should enable it to absorb enough solution so that thorough wetting takes place and the dye solution penetrates the fabric completely.

However, in the continuous method of dyeing, the following restrictions are imposed, on which a
compromise must be reached for the process to be economical as well as efficient: (i) The time of contact with the dye liquor is of the order of a fraction of a second. For example, in the Standfast Molten Metal Unit, the contact time is 0.44 sec, at 30 yd per min. and 0.11 sec. at 120 yd per min. (ii) The volume of dye bath must be as small as possible in order that there is minimum wastage of dye liquor at the end of the run. (The dye bath of the Standfast Molten Metal Unit is the smallest known in continuous dyeing operations.) (iii) The concentration of the dye solution should be much higher than that normally used. (iv) The affinity of the dyestuffs for the material produces what is known as tailing effect. (v) The dye bath temperature should be as high as possible so that the time required during the heat treatment of material is reduced to a minimum. (vi) The rate of feed must match the rate of pick-up of the dye solution by the material in order to reach (dynamic) equilibrium as early as possible. (vii) The feed liquor should not be far different in concentration from the dye bath solution; in fact, it would be preferred if the feed liquor is of the same concentration as the dye bath solution at the start.

The study of these factors with respect to dye bath construction forms an important aspect of the continuous dyeing technique for obtaining uniform shades with minimum tailing effect.

Tailing effect arises on account of the affinity of the dye for the fibre, whereby the amount of dye uptake by the fibre is always in excess of that given by the squeeze per cent. As a result of this, the concentration in the fabric suffers corresponding variation in colour. At the equilibrium stage the excess amount of dye taken up by the fabric equals the difference between the added dye and the dye in the trough, so that the fabric gets a continuous and uniform shade. The problem of tailing is related to the time required for the padding system to come to an equilibrium, or in other words, the length of cloth which must be run before a uniform colour is obtained. Table 1 illustrates this point.

The yardage required to ensure consistency of depth (within 5%) can be calculated by taking into consideration the affinity factor, dye bath capacity and rate of feed.

The affinity factor itself is a complex entity depending on a number of factors besides the intrinsic character of the dye molecule itself, e.g. concentration, temperature of the dye bath, presence of salt and other compounds in the dye bath, fabric construction and fibre properties, and padding system.

There appears to be no systematic study of each of these aspects independently. Adequate details of the work done so far are not available. Some information is available with respect to the Standfast Molten Metal Unit where the feed liquor and agitation in the bath stimulate horizontal as well as vertical movement of liquor on both sides of the cloth. Recently, the idea of high turbulence in a small narrow dye bath through jets has been introduced to overcome the difficulty of tailing in continuous ribbon dyeing. Bond’s machine utilizes jets of hot dye solution to obtain complete dyeing. The latest innovation in dye bath construction is the application of ultrasonics to obtain adequate mass transfer and penetration. This, however, is still of academic interest. Recently, the authors have applied the technique of fluidized beds of solid discrete particles where the dye solution acts as the fluidizing medium (Fig. 1).

In addition to the homogeneity of dye bath liquor and fabric penetration, which are obtained satisfactorily by adopting a few of the methods, there are other factors, such as properties of high concentrated dye solutions, dye bath capacity, rate of feed affinity and strike of the dye and fabric construction, which demand attention. All these contribute to the tailing effect, i.e., the differential shade obtained in the beginning and at the end. Mann and Marshall have carried out a fundamental study of these factors and suggested means of reducing and tailing effect. One of the suggestions pertains to the dye bath capacity and the rate of feed. According to them, the trough capacity should be as low as possible so that the cloth empties it many times, at least one and a half-times, within a short time.

It is, therefore, evident that the control of shade in a continuous dyeing system is a complex problem requiring considerable skill and knowledge on the part of the dyer. This complication would be all the more aggravated when a mixture of dyes is to be applied to the fabrics. In order to understand this complex
system in which a number of variables are involved, it is necessary to study the affinity factor under various sets of conditions that are normally encountered and evaluate their relationship with other variable factors involved.

Padding—The cloth passes through the liquid first and then through the padding mangle to obtain the requisite squeeze per cent and uniform distribution of the dye along the length and the width of the fabric. Hence, uniformity of shade depends on the efficiency of the padding mangle, particularly in a system of continuous dyeing not involving subsequent leveling off of the dye. It is only recently that the padding mangle and the padding system have received attention from the fundamental point of view. It has already been pointed out that the padding mangle also plays an important part in the tailing effect by controlling the liquor pick-up on which dye feed depends.

Heat treatment—The dye molecules which have been transferred to the requisite sites or close to the requisite sites are fixed in situ finally by heat treatment. Methods of heat treatment for the fixation of dye molecules on the fibre have considerably improved since the advent of synthetic fibres, which normally require high temperatures. Molten metal, hot oil, steaming chambers, hot flues, infra-red heating and, more recently fluidized beds (Fig. 2) are some of the methods of heat treatment. These developments have been essentially intended to meet the special demands of synthetics which are employed, mainly, as dispersed dyes. The dyes have no affinity for the fibre and are supposed to form solid solution with the fibre material. In adopting these techniques for natural fibres, a number of problems are to be faced, such as stability and behaviour of natural fibres at high temperatures, stability and behaviour of dyestuffs at high temperatures, high rates of diffusion of dyestuffs at high temperatures, and moisture versus migration of dyestuff molecules into the fibre substance.

On account of the high rates of diffusion at elevated temperatures, the actual time of heat treatment is considerably reduced; for example, for vats in pad steam process it is about 15–25 sec. and for directs, 2 to 3 min.; in the Standfast Molten Metal Unit, it is 1.6-7 sec. In the fluidized bed technique developed in the Shri Ram Institute for Industrial Research, the authors have found that heat treatment for 3 to 8 sec. (even 1 to 3 sec.) is sufficient to obtain satisfactory dyeing. In all these cases, particularly when the temperature exceeds 120–130°C., the dyeings suffer from tone change as compared to normal dyeing. Tone changes are due to decomposition or structural changes in dye molecules, e.g. possible over-reduction in the case of leuco-vat dyes or reduction of directs in the presence of cellulose and alkali. In fact, at present, manufacturers of dyestuffs supply a classified lists of temperature stable dyestuffs for the use of dyers; however, the lists cannot be used to fullest advantage where conditions are not identical with those recommended by manufacturers. It appears that the tone can be controlled, to a certain extent, by properly controlling moisture and by using protective agents, such as hydrogen peroxide, sodium percarbonate, perborate and dichromate. These agents, however, are not useful above 100°C.; further they increase the alkalinity of the material after decomposition. Ammonium salts of mineral acids are somewhat better, but not altogether satisfactory. The addition of monochrom mordants gives better results than all the protective agents recommended so far.

Textile Adhesives

Adhesive compositions are becoming increasingly used, for example in the garment manufacturing trade, for bonding fabrics together. In the garment manufacturing trade it is known to bond two fabrics together using a hot melt adhesive composition which is capable of being activated by heat and pressure in a pressing operation. However, in many cases the physical properties of the adhesive composition have to be quite specific in order to retain a satisfactory adhesive bond throughout the lifetime of a garment.

For example, an adhesive composition for use in the garment manufacturing trade may be required to retain its bond strength when a garment is being washed in warm soapy water and also when the
garment is being dry cleaned in cleaning solvents such as perchloroethylene, trichloroethylene or alcoholic spirits. In addition to the requirement of resistance to dry-cleaning solvents and to washing in warm soapy water, it is important that adhesives have a relatively wide softening point range to enable their use effectively in industrial adhesive bonding of fabric sheet, for example, in the known procedures for depositing spaced dots of adhesive from powered resin adhesive.

**Textile Adhesives**

**Diacetone Acrylamide and Aminoplasts**

A process described relates to water-soluble compositions prepared by reacting, in the presence of an alkaline reagent, an aliphatic aldehyde containing not more than 4 carbon atoms, or a reversible polymer thereof, with an N-3-oxohydrocarbon-substituted acrylamide having the formula

\[
\text{R1} \quad \text{R2} \quad \text{R3} \quad \text{R4}
\]

where each R1 is individually hydrogen or a hydrocarbon or substituted hydrocarbon radical, at least one R1 being hydrogen; each of R2 and R3 is hydrogen or a hydrocarbon or substituted hydrocarbon radical; and R4 is hydrogen, halogen or a lower alkyl or substituted lower alkyl radical; the reaction being effected in a diluent comprising (1) water, or (2) an organic liquid which is a solvent for the reactants or the product or both, or (3) a mixture of diluents 1 and 2.

For preparation of the preferred compositions of this process, from one to three and preferably all five of the R1 radicals in the N-3-oxohydrocarbon-substituted acrylamide reagent are hydrogen; R2 and R3 are lower alkyl radicals; and R4 is hydrogen or methyl. Suitable N-3-oxohydrocarbon-substituted acrylamides are described in U.S. Patents 3,277,056 and 3,425,942.

Examples are N-(1,1-dimethyl-3-oxobutyl) acrylamide, referred to as diacetone acrylamide, and N-(1,3-diphenyl-1-methyl-3-oxopropyl) acrylamide, referred to as diacetophenone acrylamide. Because diacetone acrylamide is preferred and is most readily available, it will frequently be referred to in this process. The preparation of the water-soluble compositions of this process is illustrated by the following examples. All parts and percentages are by weight unless otherwise indicated.

**Example 1:** A solution of 338 parts (2 mols) of diacetone acrylamide in 1,000 parts of water is heated to 50°C and 45 parts of a 3% aqueous solution of trisodium phosphate is added. Dropwise addition of a 37% aqueous solution of formaldehyde is then begun and is continued for one hour, a total of 650 grams (8 mols of formaldehyde) being added. During the formaldehyde addition, three further portions of trisodium phosphate solution, one of 14 parts and two of 15 parts, are added. Heating is continued for five hours after formaldehyde addition is complete, and during that time additional increments of trisodium phosphate solution are added, care being taken that the pH of the mixture never increases above 10, until a total of 299 parts have been introduced (0.16 mol or 2.0 mol percent based on formaldehyde). The solution is cooled and filtered, and volatile materials are removed by heating under vacuum at 55°C. The product is a 61% aqueous solution of the desired water-soluble composition.

**Example 2:** Following the procedure of Example 1, a similar reaction product is prepared from diacetone acrylamide and acetaldehyde.

**Example 3:** Following the procedure of Example 1, a similar reaction product is prepared from diacetone acrylamide and n-butyraldehyde.

**Example 4:** A solution of 280 parts (1.66 mols) of diacetone acrylamide in 296 parts of distilled water is heated to 33°C, and 164 parts of paraformaldehyde (5 mols based on monomeric formaldehyde) is added over 20 minutes. The solution is then heated to 47°C and 8.3 parts of a 10% aqueous solution of potassium hydroxide is added over 10 minutes. The reaction mixture is stirred and heated to 52°C over about ½ hour, at which time an exothermic reaction begins; stirring is continued and the temperature is kept at about 50°C by passing cooling water through a jacket on the reaction vessel.

At the end of the 2-hour stirring period, an additional 8.3 parts of the potassium hydroxide solution is added, and a final 8.3 parts is added after a further 2-hour stirring period (total 0.9 mol percent based on formaldehyde added).
formaldehyde). The mixture is stirred for an additional 2 hours, cooled to 24°C and filtered. The product, a 55% aqueous solution of the desired water-soluble composition, contains 3.04% nitrogen.

Example 5: To a solution of 644 parts (3.81 mols) of diacetone acrylamide in 681 parts of water, at 31°C, is added, with stirring, 372 parts of paraformaldehyde (11.3 mols based on monomeric formaldehyde). The mixture is heated to 43°C and 19 parts of a 10% aqueous solution of potassium hydroxide is added. The mixture is further heated, with stirring, to 48° to 55°C and maintained at this temperature for 2 hours. An additional 10 parts of potassium hydroxide solution is then added and stirring is continued for 2 hours, followed by addition of a third 19 ml portion of potassium hydroxide solution (total 0.87 mol percent based on formaldehyde) and stirring for 2 more hours. The solution is then cooled to 29°C, 0.044 part of methylhydroquinone is added and the mixture is filtered. The product, a 53% aqueous solution of the desired water-soluble composition, contains 3.04% nitrogen.

Example 6: A mixture of 1,352 parts (8 mols) of diacetone acrylamide, 1,136 parts of methanol and 480 parts of a solution comprising 55% formaldehyde (8.8 mols of formaldehyde), 35% methanol and 10% water is heated to 44°C, and 10 parts of a 10% solution of potassium hydroxide in methanol (0.2 mol percent of potassium hydroxide based on formaldehyde) is added. The mixture is heated at 44° to 47°C for 7 hours, with stirring, and is then stripped of volatile materials by distillation at 48°C/4 torr. The water-soluble product contains 7.08% nitrogen.

Example 7: Following the procedure of Example 6, a water-soluble product containing 6.16% nitrogen is obtained from 1,014 parts (6 mols of diacetone acrylamide, 1,706 parts of methanol, 491 parts (9.0 mols of formaldehyde) of formaldehyde-methanol-water solution, and 10 parts of methanolic potassium hydroxide (0.2 mol percent potassium hydroxide based on formaldehyde).

Example 8: Following the procedure of Example 6, a water-soluble product containing 6.38% nitrogen is obtained from 1,014 parts (6 mols of diacetone acrylamide, 1,767 parts of methanol, 654 parts (12 mols of formaldehyde) of formaldehyde-methanol-water solution, and 10 parts of methanolic potassium hydroxide (0.15 mol percent potassium hydroxide based on formaldehyde).

Example 9: A mixture of 291 parts of ethyl acrylate, 16 parts of the product of Example 4, 596 parts of water and 90 parts of a 21% aqueous solution of a sodium alkaryl polyether sulfate anionic emulsifier sold under the trade name Triton X-301 is purged with nitrogen for 45 minutes, after which a solution of 1.5 parts of ammonium persulfate in 10 parts of water and a solution of 0.3 part of sodium formaldehyde sulfoxylate in 15 parts of water are added. The reaction vessel is cooled as the mixture is stirred and an exothermic reaction takes place which causes the temperature to rise the 59°C. After the 10 minutes an additional solution of 0.3 part of sodium formaldehyde sulfoxylate in three parts of water is added and the mixture is filtered, yielding the desired copolymer latex.

Example 10: A mixture of 87 grams of diacetone acrylamide, 30 grams of the product of Example 6, 180 grams of butyl acrylate, 3 grams of acrylic acid, 418 grams of water and 34 grams of an anionic emulsifier sold under the trade name Abex 18S is purged with nitrogen. To the mixture is added 5 ml of a 10% aqueous solution of sulfuric acid, 1.0 gram of sodium formaldehyde sulfoxylate and 1.5 grams of ammonium persulfate. The mixture is stirred under nitrogen for about 15 minutes and then heated to 72°C, after which 1 ml of t-butyl hydroperoxide is added. Heating is continued at about 60° to 65°C for 2 hours. The desired tetrapolymer latex is then filtered through cheese cloth and neutralized with 10% aqueous ammonia solution.

Example 11: Following the procedure of Example 10, a tetrapolymer latex is prepared from 30 parts of diacetone acrylamide, 30 parts of the product of Example 8, 120 parts of butyl acrylate, 20 parts of methacrylic acid and 283 parts of water, and is then neutralized with 10% aqueous ammonia solution.

Example 12: Following the procedure of Example 10, a terpolymer latex is prepared from 70 parts of the product of Example 7, 110 parts of butyl acrylate, 20 parts of methacrylic acid and 280 parts of water,
and is subsequently neutralized with 28% aqueous ammonia solution.

Example 13: A pressure bottle is charged with 25 parts of styrene, 70 parts of butadiene, 9.6 parts of the product of Example 5, 200 parts of butadiene, 0.2 part of potassium persulfate, 4 parts of diamy sodium sulfosuccinate, 0.25 part of sodium naphthalene sulfonate emulsifier sold under the trade name Tamol N, 0.5 part of cumene hydroperoxide, 0.5 part of t-dodecyl mercaptan and 0.2 part of sodium formaldehyde sulfoxylate. The bottle is sealed and agitated for 5 hours at 50°C; it is then opened and 2 parts of an alkylphenyl polyethoxyethanol nonionic emulsifier sold under the trade name Triton X-405, 7.8 parts of water and 0.2 part of sodium diethyl dithiocarbamate are added. Volatile materials are removed by steam stripping, yielding the desired terpolymer latex.

Example 14: Following the procedure of Example 13, a tetrapolymer latex is prepared from 15 parts of styrene, 70 parts of butadiene, 10 parts of diacetone acrylamide, 9.6 parts of the product of Example 5 and 200 parts of water.

Example 15: A reaction flask is charged with 500 parts of water, 36 parts of styrene, 36 parts of butyl acrylate, 4 parts of the product of Example 4, 1 part of acrylic acid, 5 parts each of an oxyethylated alkylphenol water soluble emulsifier solid under the trade name Igepal CO-710 and a similar oil-soluble emulsifier sold under the trade name Igepal CO-520 and 2.5 parts of sodium lauryl sulfate. The mixture is purged with nitrogen and stirred as a solution of 0.2 part of ammonium persulfate in 5 parts of water and a solution of 0.2 part of sodium formaldehyde sulfoxylate in 5 parts of water are added. Stirring is continued as the mixture is heated to 68°C, and there are simultaneously added (1) a mixture of 410 parts of water, 286 parts of styrene, 286 parts of butyl acrylate, 36 parts of the product of Example 4, 6 parts of acrylic acid, 5 parts each of Igepal CO-710 and Igepal CO-520, and 1 part of sodium lauryl sulfate; (2) a solution of 1.4 parts of ammonium persulfate in 50 parts of water; and (3) a solution of 1.4 parts of sodium formaldehyde sulfoxylate in 50 parts of water. The addition takes place over 1 hour at 68° to 72°C. Stirring is continued at 72° to 80°C as additional portions of ammonium persulfate and sodium formaldehyde sulfoxylate are added. The mixture is cooled to room temperature and filtered through cheesecloth, a solution of Igepal CO-710 in 25 parts of water and a solution of Triton X-405 in 7 parts of water are added, and the material is stirred briefly. The product is the desired tetrapolymer latex.

The addition polymers of this process, particularly latexes thereof, have a self-cross-linking properties which make them particularly useful as adhesives. Because of these self-crosslinking properties, the polymers may be cured under acidic (preferably) or alkaline conditions at temperatures from room temperature to about 200°C to form adherent films with a high percentage of acetone insolubles. Such polymers are especially useful as laminating adhesives and binders for textiles and nonwoven fabrics. It is possible to formulate an adhesive in which the only ingredient present in substantial amounts in the polymer latex of this process, with the optional presence of such substances as thickeners, antifoam agents, protective colloids, pigments and the like which are known in the art. Particularly useful for this purpose are polymers containing units derived from an acidic compound such as acrylic acid.

For example, the polymer of Example 10, 11 and 12 may be combined with a 5% aqueous hydroxyethylcellulose solution (as a protective colloid) in an amount to provide 4.5 parts of hydroxyethylcellulose per 100 parts of polymer to form a composition suitable for use as an adhesive. However, such adhesives ordinarily cure only at undesirably high temperatures, frequently above 150°C. The preferred adhesive compositions additionally contain at least one substance selected from the group consisting of alkaline reagents (e.g., sodium hydroxide, potassium hydroxide) and the aminoplast compositions previously described herein. Both of these substances may be present, but it is usually satisfactory to use only in an amount of about 0.5 to 10.0 parts per 100 parts of the polymer of this process.
It is particularly preferred to use hexamethoxy-methylmelamine. Typical adhesive compositions containing the addition polymers are listed below.

The utility of the adhesive compositions containing the polymers of this process is illustrated by a procedure in which the adhesive is applied in a checkered pattern by pyramidal dots from an engraved roll onto a strip of cotton cloth resting on a piece of soft rubber. A layer of tricot is placed over the adhesive and a cylindrical weight is rolled over the laminate to assure bonding. The laminate is then placed in a forced-air oven, tricot side down, at 150°C for 3 minutes. The cured laminates are found to have excellent peel resistance, dry and wet strength and "hand". Latexes of the addition polymers containing units derived from styrene and butadiene (e.g., the products of Examples 13 and 14) may be used as glass-to-rubber adhesives.

Lactam Copolyamides

Scientist have found that acceptable bond strength is fabric to fabric bonds and good resistance to washing in warm soapy water and to dry cleaning may be obtained by use of an adhesive composition comprising a polyamide formed from a mixture in controlled proportions of at least one lactam, a mixture of aliphatic dicarboxylic acids and at least one diamine. The components are selected to give polymer molecules having a degree of irregularity which interferes with crystallization and contribute to a substantial degree amorphous characteristics giving a wide melting point range.

In addition, the compounds selected for copolymerization include components having a relatively large number of carbon atoms in chains in repeating units of the copolyamide molecular chain to impart improved wash resistance to the composition together with components giving improved resistance to attack by drycleaning solvents. Also, by balancing the range of relative proportions and the conditions of polymerization to control the molecular weight and softening point range of the resulting copolyamide material having physical properties enabling it when reduced to powdered condition to retain this condition without undue lumping while at the same time having a relatively wide range of softening or melting temperatures particularly avoiding critical temperature control and other handling problems encountered in use of the material for the hot melt adhesive between, for example, layers of fabric.

Example: A series of copolyamides were prepared by the procedure set forth below using reagent mixtures and forming products having the properties listed in the table on next page.

The procedure used for making the copolyamide involved melting the lactam and the dicarboxylic acid components together in a reaction vessel. Thereafter, diamine was added and the temperature allowed to rise to from 100° to 120°C. The reaction mixture was heated under reflux conditions until salt formation was completed and at this point the temperature was raised to 200°C to eliminate water. The temperature of 200°C was maintained for 2 hours and then a vacumm was applied to the reaction mixture and heating continued for a further hour at 200°C. At this point, polymerization was complete and the resinous polymeric materials was poured out into a casting tray. The resinous material was cryogenically ground and screened to form a uniform powder having a particle size of from 60 to 210 microns. The copolyamide powders were used to bond pieces of fabric and the bonds between the pieces of fabric were tested by the following procedure.

Flame Retardants For Textile

Hazards associated with the ready combustibility of cellulosic materials were recognized as early as the 4th century BC, when Aeneas is said to have recommended treatment of wood with vinegar to impart fire resistance. The annals of Claudius record that wooden storming towers used in the siege of Piraeus in 83 BC were treated with a solution of alum to protect them against fire.

The technique of imparting flame resistance to textile fabrics is relatively new. Among the earliest
references is an article by Sabattini published in 1638. Recognizing a need to prevent fire, he suggested that clay or gypsum pigments be added to the paint used for theater scenery to impart some flame resistance. Perhaps the first noteworthy recorded attempt to impart flame resistance to cellulose was made in England in 1735 when Obadiah Wyld was granted a patent for a flame-retardant mixture containing alum, ferrous sulfate, and borax.

In France in 1821, Gay-Lussac developed a flame-resistant finish by treating linen and jute fabrics with a mixture of ammonium phosphate, ammonium chloride, and borax.

The first successful, launder-resistant, flame-retardant finish for fabric was based on the work of Perkin who precipitated stannic oxide within the fiber. This fabric was flame resistant but afterglow was severe and persistent enough to completely consume the fabric.

Flame retardants are mainly used on cottons and rayons. Fabrics made from wool (qv), silk (qv) and protein-like synthetic polymers are not considered sufficiently combustible, for the most part, to warrant the need for flame-retardant finishes (see Biopolymers; Textiles).

Since World War II the flammability of textiles of all types has received greatly increased attention, spurred by the Conference on Burns and Flame Retardant Fabric in 1966 and by the 1967 amendment to the Flammable Fabrics Act of 1953. Flammability standards were established by the Department of Commerce and enforced by the Federal Trade Commission. This responsibility was taken over by the Consumer Product Safety Commission when it was created in 1973.

The term used in connection with flame-resistant fabrics are sometimes confusing. Fire resistance and flame resistance are often used in the same context as the terms fireproof or flameproof. A textile that is flame resistant or fire resistant does not continue to burn or glow once the source of ignition has been removed, although there is some change in the physical and chemical characteristics. Fireproof or flameproof, on the other hand, refer to material that is totally resistant to fire or flame. No appreciable change in the physical or chemical properties is noted. Asbestos is an example of a fireproof material.

Most organic fibers undergo a glowing action after the flame has been extinguished, and flame-resistant fabrics should also be glow resistant. Afterglow may cause as much damage as the flaming itself since it can completely consume the fabric. The burning (decomposition) temperature of cellulose is about 230°C, whereas afterglow temperature is approximately 345°C.

Chemical modification of cellulose with fire retardants gives products whose resistance to laundering and weathering is superior to that of finishes based on the physical deposition of the flame retardant within the fabric, yarn, or fiber. The reactions involved are either esterification or etherification. The latter is preferred because ether linkages are more stable to hydrolysis.

**Flame Resistance**

The flame resistance of a textile fiber is affected by the chemical nature of the fiber; ease of combustion; fabric weight and construction; efficiency of the flame retardant; environment; and laundering conditions.

Fire-resistant characteristics can change significantly when treated fabric is exposed to sunlight, followed by laundering, even though repeated washing and tumble drying of samples of the same specimen did not indicate any significant changes, especially in the durability of the finish. Dry heat alone, followed by laundering or autoclaving can also have a deleterious effect.

Fibers are classified into natural fibers, e.g. cotton, flax, silk, or wool; regenerated fibers, e.g. rayon; synthetic fibers, e.g., nylons, vinyls, polester, acrylics; and inorganic fibers, e.g. glass or asbestos. Combustibility depends on chemical makeup and whether the fiber is inorganic, organic or a mixture of both.
The weight and construction of the fabric affect its burning rate and ease of ignition. Lightweight, loose-weave fabrics usually burn faster than heavier-weight fabrics; therefore, a higher weight add-on of fire retardant is needed to impart adequate flame resistance.

Phosphorus-containing materials are by far the most important class of compounds used to impart durable flame resistant to cellulose. They usually contain either nitrogen or bromine and sometimes both. A combination of urea and phosphoric acid imparts flame resistance to cotton fabrics at a lower add-on than when the acid or urea is used alone. Other nitrogenous compounds, such as guanidine, or guanylurea, could be used instead of urea. Amide and amine nitrogen generally increase flame resistance, whereas nitrile nitrogen can detract from the flame resistance contributed by phosphorus. The most efficient flame-retardant systems contain two retardants, one acting in the solid and the other in the vapor phase. Bromine in flame-resistant fabric escapes from the tar to the vapor phase during pyrolysis in air. It appears to have little or no effect on the amount of phosphorus remaining in the char. Bromine contributes flame resistant almost completely in the vapor phase.

Nitrogen when used in conjunction with phosphorus compounds has synergistic effects. Phosphorus content can be reduced without changing the efficiency of the flame retardant.

The temperature of the environment influences the burning characteristics of fabric as measured by the oxygen index (OI). This is true for untreated as well as flame-retardant fabrics. For example, the OI value of untreated fabric is 0.18 when burned at 25°C and 0.14 when burned at 150°C. For flame-retardant fabric, an OI value of 0.35 at 25°C may be reduced to 0.27 when burned at 150°C. Sunlight and heat can also destroy some flame retardancy, especially when followed by laundering or autoclaving. The moisture content of fabric can also affect flame retardancy.

Fire retardancy of a treated cellulosic fabric is reduced when the retardant contains acid groups and the treated fabric is soaked or laundered in water containing calcium, magnesium, or alkali metal ions. Phosphate and carbonate-based detergents affect durability of fire retardants. Soap-based detergents can result in a substantial loss of fire resistance because of deposit of fatty acid salts. Phosphorus based flame retardants are adversely affected by water hardness and sodium hypochlorite.

Mechanisms: Cellulose, as such, has no appreciable vapor pressure and does not burn. However, on exposure to high temperatures it decomposes exothermically into flammable compounds causing further degradation and decomposition until complete treated and flame-retardant-treated cellulose. Decomposition takes place in two stages. First, thermal decomposition causes cellulose to decompose heterogeneously into gaseous, liquid, tarry, and solid products. The flammable gases thus produced ignite, causing the liquids and tars to volatilize to some extent. This produces additional volatile fractions which ignite and produce a carbonized residue which does not burn readily. This process continues until only carbonaceous material remains. After the flame has subsided, the second stage begins. the residual carbonized residue slowly oxidizes and glowing continues until carbonaceous char is consumed.

Cotton (qv) treated with an effective flame retardant forms, in general, the same decomposition products upon burning as untreated cotton; however, the amount of tar is greatly reduced with a corresponding increase in the solid char. Consequently, as decomposition takes place, smaller amounts of the flammable gases are available from the tar, and greater amounts of nonflammable gases from the decomposition of the char fraction.

Effective glow retardant chemicals, such as compounds containing phosphorus, cause the first reactions to be prevalent. Oxidation of carbon monoxide is not sufficiently exothermic to maintain afterglow of the char.

Imparting flame resistance to cellulose has been explained by the following theories:

Coating theory: As early as 1821, Gay-Lussac suggested that fire resistance was due to formation of a layer of fusible materials which melted and formed a coating thereby excluding the air necessary for the
propagation of a flame. This was based on the efficiency of some easily fusible salts as flame retardants. Carbonates, borates, and ammonium salts are good examples of coating materials that produce a foam on the fiber by liberation of gases such as carbon dioxide, water vapor, ammonia, etc.

**Gas theory:** The flame retardant produces noncombustible gases at burning temperature which dilute the flammable gases produced by decomposition of the cellulose to a concentration below the flaming limit.

**Thermal theory:** Heat input from a source is dissipated by an endothermic change in the retardant and the heat supplied from the source is conducted away from the fibres so rapidly that the fabric never reaches temperature of combustion.

**Chemical theory:** Strong acids, bases, metal oxides, and oxidants that tend to degrade cellulose, especially under the influence of heat, usually impart some degree of flame resistance to cellulose. This is also true of the more efficient flame retardants, such as phosphoric and sulfuric acid, which are good dehydrating agents. When this happens, cellulose on combustion produces mainly carbon and water rather than carbon dioxide and water.

Flame retardants for cotton may possibly act through a dehydration process by Lewis acid or base formation through a carbonium ion or carbanion mechanism. This theory is being further investigated.

Earlier theories suggested that flame-retarded cellulose decomposed at high temperature to l-glucosan which in turn broke down to form other volatile products which were highly flammable. However, if bases are present in the fabric during burning, dehydrocellulose is formed by a base-catalyzed dehydration followed by char formation. Base-catalyzed at an energy level below that required of l-glucosan by propagating structural changes at an energy level below that required to convert the coformers of the glucopyranose ring.

**Durability**

**Nondurable, Finishes:** Flame-retardant finishes that are not durable to laundering and leaching are, in general, relatively inexpensive and efficient. In some cases, mixtures of two or more salts are much more effective than any one of the components alone. For example, an add-on of 60% of borax $\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$ is required to prevent fabric from burning. Boric acid, $\text{H}_3\text{BO}_3$, by itself, is ineffective as a flame retardant even in the amounts that equal the weight of the fabric. However, a mixture of seven parts borax and three parts boric acid imparts flame resistance to a fabric with as little as 6½% add-on.

The water-soluble flame retardants are most easily applied by impregnating the fabric with a water solution of the retardant, followed by drying. Adjustment of the concentration and regulation of the fabric wet pickup controls the amount of retardant deposited in the fabric. Fabric can be processed on a finishing range consisting of any convenient means of wetting the fabric with the solution, such as a padder or dip tank, followed by a drying on cans, in an oven, on a tenter frame, or merely by tumbling in a mechanical dryer. Water-soluble flame retardants also may be applied by spraying or brushing, or dipping fabrics, or as a final rinse in a commercial or home laundry. The water-soluble flame retardants, most widely used for textiles are listed in Table 1. Less commonly used are sulfamates of urea or other amides and amines; aliphatic amine phosphates, such as triethanolamine phosphate [10017-56-8], phosphamic acid [2817-45-0] (monooimido phosphoric acid), $\text{H}_2\text{PO}_3\text{NH}_2$, and its salts; and alkylamine bromides, phosphates, and borates.

**Semidurable Finishes:** Semidurable fire retardants are those that resist removal for one to about 15 launderings. Such retardants are adequate for applications such as drapes, upholstery, and mattress ticking. If they are sufficiently resistant to sunlight or can be easily protected from actinic degradation, they can also be applied to outdoor textile products.

These codeposits and flame and glow resistance properties to textile fabrics. However, some insoluble deposits may also degrade the fabrics. Codeposits quite frequently improve glow resistance. They are usually more soluble than the deposit responsible for flame resistance and are more easily removed
during the laundering process.

There are several methods for introducing the insoluble deposits into the fabric structure. Most generally used is the multiple-bath method, in which the fabric is first impregnated with a water-soluble salt or salts in one bath, and is then passed into a second bath which contains the precipitant.

Most semidurable retardants are used on cotton and are based on a combination of phosphorus and nitrogen compounds.

**Durable Finishes:** Earlier studies to produce durable flame retardants for cellulose were based on treatment with inorganic compounds containing antimony and titanium. Numerous patents were issued based on these types of treatments, e.g. DuPont’s Erifon process and the Titanox FR process of the Titanium Pigment Corporation.

In the Erifon process titanium and antimony oxychlorides were applied from acid solution (pH4) to fabric, which was then neutralized by passing through a solution of sodium carbonate, followed by rinsing and drying. Fabrics thus finished exhibited good flame resistance but also considerable afterglow. Some fabric characteristics were changed by this treatment. A large amount of tent fabric was treated by this type of process for the military service. However, it has now been replaced by flame retardants based on phosphorus.

The basic chemicals used in the Titanox FR process were titanium acetate chloride and antimony oxychloride. As with the Erifon process, it was difficult to process the fabric without dulling its appearance.

Excellent fire-resistant fabric was obtained by treating fabric with a suspension or emulsion fire-retardant salts or oxides, eg, antimony oxide, with a chlorinated organic vehicle, such as chlorinated paraffin. Antimony oxide alone is only a poor flame retardant. When used, however, in conjunction with a chlorinated compound, which can form hydrochloric acid on heating, a very good flame retardant is produced.

The abbreviation, FWWMR, for fire, water, weather and mildew resistance has frequently been used to describe treatment with a chlorinated organic metal oxide. A plasticizer, coloring pigments, fillers, stabilizers, or fungicides are usually added. However, hand, drape, flexibility, and color of the fabric are more affected by this type of finish than by other flame retardants. Durability of this finish is good and fabric processed properly retains its flame resistance after four to five years of outdoor exposure. This type finish is well suited for very heavy fabrics, e.g. tents, tarpaulins, or awnings, but not for clothing or interior decorating fabrics. The metal oxides can be fixed to cotton by use of resins, e.g. vinylacetate–chloride copolymers (vinylite VYHH) or PVC.

A flame retardant has been developed based on an oil–water emulsion containing a plasticizer (PVC latex) and antimony oxide. High add-ons are necessary to impart adequate flame resistance but the strength of the fabric is little affected.

### Halogenated Flame Retards

#### Halogenated Flame Retardants

The development and extensive use of synthetic polymers in both old and new types of applications has intensified the concern for combustibility. Although these new polymers are not necessarily more flammable than natural polymers, they are more readily used in forms, e.g., foams, electrical applications, etc, that can result in an increased fire control problem.

Along with the development of many synthetic polymer systems during the 1930s and 1940s, a significant advance in the science of imparting flame resistance occurred, i.e., the use of halogenated organic materials to impart ignition resistance to these new polymer systems.

In early plastics applications, the small size of fabricated articles and the relative scarcity of these articles made fire retardancy a secondary consideration. Advances in plastics technology have led to
increasing large-scale applications, especially in the construction industry. Since many polymers have fuel values (heats of combustion) comparable to common fuels, eg, wood, oil, alcohol, etc, it is readily understandable that they contribute to the burning process in a typical fire.

Commercial halogenated products used as flame-retardants for plastics currently in use are mainly compounds containing high (50–85 wt %) levels of either chlorine or bromine, i.e., decabromodiphenyl oxide [1163-19-5], chlorendic acid [115-28-6], tetrabromophthalic anhydride [632-79-1], etc. These materials fall into two distinct types: additives and reactives. The additives have the advantage of being readily added to a polymer by mechanical means with a minimum of reformulation being required. The reactives, on the other hand, require the development of essentially new polymer systems.

Only massive polymer forms are considered, though the materials and concepts discussed are almost similarly applicable to fibers, fabrics, coatings, and elastomers. Halogenated phosphorus compounds are included under Flame retardants—phosphorus compounds.

Principles of Developing Flame-Retardant Polymers

Any discussion of the principles of developing flame-retardant polymer systems must acknowledge the chaotic situation that exists at present. This situation has arisen for a variety of reasons: technical, economic, legal, and semantic.

The semantic problem is the worst in that it is at the root of most of the other problems and is caused by the fact that the term fire or flame retardant may be perceived in a variety of ways depending upon the user’s viewpoint. The term, as defined above, means simply that some change has been made in polymer system so that it will pass one or more of at least a hundred different flammability tests. These tests are normally designed to minimize, but not eliminate, the fire risk associated with the use of a polymer in some specific use or product. As a consequence, a modification of a polymer that makes it suitable for one use does not necessarily make it suitable for others. There is no single fire-retardant chemical or method that is applicable to all polymer systems or even to all uses of a single polymer.

It is, therefore, necessary that early in the development of a flame-retardant polymer system the question “Why?” is answered before much effort it put into answering the question “How?”.

It is not unusual to see many compounds proposed as flame-retardant chemicals that are clearly unusable in any practical sense, but that allow a polymer system to pass a specific flammability test. A polymer system can be easily modified so that it can be called “flame-retardant” by some “test”. It is difficult, however, to do so and keep a polymer system that is low-cost, environmentally and physiologically acceptable, and also mechanically and esthetically not too dissimilar from nonfire-retardant counterparts.

One of the most common approaches used to modify the burning properties of polymers at the present time is by incorporation of halogen into the polymer matrix, either directly or through the use of halogenated additives. The usual rationale for the use of the halogens as flame retardants is based on the theory that they function in the gas phase as radical traps. It is generally agreed that the combustion of gaseous fuels is a high temperature process which proceeds via a free radical mechanism.

In the radical-trap theory of flame inhibition it is thought that equations 6–10 effectively compete with equations 2–5 for those radical species that are critical for flame propagation, i.e., ·OH and ·O·, thereby slowing the rate of energy production and resulting in the extinction of the flame. Hydrogen fluoride does not significantly enter into the flame chemistry, thus fully fluorinated compounds are generally considered to be ineffective as flame-retardant agents. The radical-trap theory of flame inhibition, although attractive in that it can be adapted to any situation, tends to lead to the belief that the simple inclusion of small amounts of halogen into a polymer system will render the system flame retardant.

A recent physical theory of flame suppression by the halogens, although conceding that the halogens enter into flame chemistry, suggests that this participation per se cannot be the primary mechanism by which the halogens function. Rather, it is postulated that the halogens act by altering the physical
properties, i.e., the density and mass heat capacity of the gaseous fuel–oxidant mixture so that flame propagation is effectively prevented. The physical theory is primarily based on the observations that any gaseous mixture of fuel and halogenated agent generally propagates flame when mixed with air as long as the mass fraction of halogen in the mixture is less than ca 0.7, and the relative effectiveness of the halogens is directly proportional to their atomic weights, i.e., F:Cl:Br:I = 1.0:1.9:4.2:6.7. The halogenated agents probably act by the same basic mechanisms as the inert gases, i.e., CO2 N2, etc, and their suppressant effective are additive to those of the inert gases.

Mo is the mass fraction of oxygen in the combustion zone; Hc is the net heat of combustion of the sample (J/g); r is the stoichiometric mass oxygen/fuel ratio; Cp is the specific heat of the gases in the combustion zone Ts is the surface temperature of the sample (°C), Ta is the ambient temperature (°C); and HG is the apparent heat of gasification (J/g). The B number contains the fundamental properties of the polymeric materials. Thus the mass burning rate or burning intensity can be related to the fundamental properties of the material.

When applied to liquid fuels, the Spalding B number in its simplest form can be visualized as the ratio of the heat of combustion and the heat of vaporization (DHc/DHv). Table 1 shows the significance of this ratio applied to several halogen-containing fuels. In Table 1 the flash and fire points are expressed both in °C, as normally reported, and as the weight of compound present in the gas phase over the surface of the liquid at this temperature (mg/L). The introduction of halogen has a lesser effect upon DHv per milligram of compound evaporated. The ratio DHc/DHv decreases with added halogen indicating that less energy is available from the flame for gasification, and, in order to keep the flame burning, additional heat from some outside source is required. DHv is the amount of heat required to vaporize the weight of fuel (latent heat of vaporization) present in the gas phase at the appropriate flash and fire points after the fuels have been raised to these temperature by the outside source. Note the large increase in mass that must be vaporized in order to obtain sustained burning in the case of bromobenzene, at least 100 times the mass that must be vaporized in the case of benzene itself.

The physical theory apparently accounts for the effects seen when halogenated agents are used as flame retardants. In view of the fact that the halogen content of a typical plastic is generally ca 1–30 wt %, it is obvious that if the typical polymer were totally vaporized the gases given off would be quite capable of flame propagation.

In order to visualize the role of halogen it is necessary to examine the heat balance that occurs at the surface of the polymer. Figure 1 shows a schematic of this balance. Heat received by the polymer surface may arise either as a heat flux from the flame (QT) or as an externally applied heat flux (QE) derived from another source. Heat is lost either as the heat required for gasification (QG) of the polymer or as heat lost (QL) through radiation, conduction, convection, dripping, etc. QT and QG are agent dependent, whereas QE is obviously agent independent, except in char-forming systems. QL may be agent dependent if the agent acts by increasing the drip rate of the burning polymer. Halogenated agents affect the heat balance through QT, QG, and QL. Although phosphorus may act in the gas phase, it appears to be the most important element affecting QG and QE through char formation.

Qualitatively, the burning process involves heating of the substrate to a temperature high enough to drive off flammable vapors. When the rate of vapor evolution becomes high enough to generate a flammable mixture, the mixture ignites. If the rate of vapor or gas evolution becomes sufficiently high, the heat produced by the combustion process may return enough heat to the substrate so that the evolution of fuel becomes self-sustaining.

When a flame retardant that acts in the vapor phase is added to the system, part of the vapor that distills from the polymer does not contribute to the heat of combustion but results only in a reduction in the mass fractions of the oxygen and fuel in the combustion zone. Hence, there is an increase in the total mass
of material that must be vaporized per unit time in order to keep the fire burning. A corresponding increase in the amount of energy must be added to the system from an external heat source (QE, Figure 1) in order to vaporize the extra material.

Both dripping and char formation interfere with the energy feedback cycle (QT and QE) and consequently cause an increase in the intensity of the external heat flux required to balance the energy–fuel cycle.

Where the flame is actively spreading over the surface of a material, the elemental composition of the vapor being evolved ahead of the moving flame is not necessarily the same as the elemental composition of the polymer. The composition of the vapors may vary considerably between the temperature at which the material first begins to evolve vapors and the temperature at which the rate of evolution supports the flame. With this type of dynamic burning condition, changes in the substrate and the structure of the agent are more important than they are under steady-state conditions.

There are five fundamental methods used to fire-retard both natural and synthetic polymer systems. They are:

Raise the decomposition temperature of the polymer. This is generally accomplished by increasing the cross-linking density of the polymer, as with ladder polymers (increase QG).

Reduce the fuel content of the system. This approach generally involves halogenating the polymer backbone, adding halogenated additives, adding inert fillers, or by resorting to inorganic systems (increase QG, decrease QT).

Induce polymer flow by selective chain scission. This approach is generally applicable to thermoplastic polymer systems where interrupting the polymer backbone results in reduction of the viscosity of the polymer and promotes dripping (increase QL).

Induce selective decomposition pathways. This method is most applicable to cellulosics where the introduction of phosphorus compounds generates phosphorus acids which catalyze the loss of water and the retention of the carbon as char (increase QG, decrease QT).

Mechanical means include (1) bonding a nonflammable skin on the polymer, (2) covering the polymer with an intumescent coating, (3) design of the system, and (4) the use of sprinklers (decrease QE).

Antimony–Halogen Synergism. Antimony oxide, a commonly employed fire retardant adjunct for halogen-containing polymer systems, is usually employed as a means of reducing the halogen levels required to obtain a given degree of flame retardancy with the polymer system. This reduction is often desirable since the required halogen content for the system may be so high that it affects the physical properties of the system. In other cases, the antimony oxide is used simply to give a more cost-effective system.

Antimony–halogen systems have been widely studied in attempts to explain the apparent, synergistic effects obtained with this combination of elements. No completely satisfactory theory is available as yet, but it is generally agreed that the active agents, antimony trihalides or antimony oxyhalides, act principally in the gas phase. As with the halogens, it is generally postulated that the antimony halides act as radical traps.

Small scale tests show that the optimum halogen (Cl, Br)/antimony atom ratio in most systems is 3/1, corresponding to the atom ratio found in the antimony trihalides, i.e., SbCl3, SbBr3. On the usual weight basis, this corresponds to a ratio of ca 0.9/1 for the chlorine–antimony system and ca 2/1 for the bromine–antimony systems.

Although the antimony halides appear to act principally in the gas phase, some effect on the condensed-phase chemistry cannot be ruled out. Antimony–halogen flame-retardant compositions usually produce a carbonaceous residue, even in polymers such as polypropylene, which produces none in the absence of fire retardants. The production of the carbonaceous residue probably results from the antimony trihalides, strong Lewis acid catalysts, which are capable of promoting the dehydrohalogenation of organic
halides, and coupling and rearrangement reactions in organic systems.

**Anatomy and other Inorganic Compounds**

In many polymers, the high concentrations of halogenated organic compounds, needed to impart flame retardancy, adversely affects their physical properties. In practice, halogen-containing flame retardants are formulated with inorganic compounds that behave synergistically with the halogen. This enables formulators to use less additives without diminishing flame retardance. Indeed, in many instances, flame retardancy is improved when inorganic halogen synergists are used.

**Antimony Compounds**

**Antimony Trioxide:** In 1979 approximately 15,900 metric tons of antimony trioxide [1309–64–4] (commonly referred to as antimony oxide) was used to impart flame retardance to a variety of plastics. Antimony trioxide is manufactured by oxidizing molten antimony sulfide ore and/or antimony metal in air at 600–800°C(1). Typical properties for antimony trioxide are listed in Table 1 (see Antimony compounds).

Antimony trioxide is a white pigment (qv). Its pigment strength is a function of the average particle size and the particle size distribution. Particle size can be controlled during its manufacture to produce either a high tint or a low tint product. The difference in the particle size and particle size distribution between high tint and low tint antimony trioxide is illustrated in Figure 1. Both grades have the same flame inhibiting efficacy but have different effects on pigmentation and physical properties. Domestic products and trade names of antimony trioxide are summarized in Table 2. Special grades are available at higher costs. They include White Star S15 from the Harshaw Chemical Company and ultra-fine antimony oxide from PPG Industries.

**Antimony Trioxide in Cellulosics:** Antimony trioxide can be used as a condensed-phase flame retardant in cellulosic materials. In these substrates, it reacts endothermically with the hydroxyl groups and forms a variety of products. The endothermic reaction absorbs heat needed to propagate the flame. The products formed are difficult to ignite and shield the underlying cellulose from the flame, minimizing pyrolytic and oxidative degradation.

**Antimony Pentoxide:** Antimony pentoxide [1313-60-9] is manufactured by the oxidation of antimony trioxide with nitrates or peroxides. For Sb2O5 the wt% of antimony is 72.8 and the specific gravity is 3.8.

Commercially, antimony pentoxide is primarily available as a stable colloid (Nyacol, Inc.) or as a redispersible powder (Nyasol, Inc.; PPG Industries, Inc.) It is significantly more expensive than antimony trioxide and is designed primarily for highly specialized applications. Antimony pentoxide manufacturers suggests fiber and fabric treatment applications as a potential area for its use. The redispersible powder form of antimony pentoxide, which is also recommended for plastics, contains 88% antimony pentoxide, and 12% dispersing agents. Care must be exercised when this product is incorporated into plastic since the dispersing agents can adversely affect the thermal stability and physical properties.

**Sodium Antimonate:** Sodium antimonate [15593-75-6], Na2OSb2O5.½H2O, is a free-flowing white powder made by the oxidation of antimony trioxide in a basic medium. A few of its properties are shown in Table 2.

The pigmenting strength of sodium antimonate is less than antimony trioxide. It is recommended for formulations in which deep tone colours are required. Because it contains 62 wt % antimony, somewhat higher concentrations are needed to make it as effective as antimony trioxide which has 83 wt % antimony.

**Mixed Metal Antimony Compounds:** Recent developments in inorganic flame retardant synergists have centered on mixed products that contain antimony and other metals which reported give excellent performance at reduced cost.

Thermoguard CPA (M & T Chemical, Inc.) appears to be as effective as antimony trioxide in most flame retardant applications, and has a significantly lower price. Although it contains a lower level of
antimony compared to antimony trioxide, other metals contained in the product significantly boost its flame retarding properties.

NL Industries has developed a series of antimony–silico complex under the trade name Oncor. These products contain up to 50% antimony trioxide. They are less opacifying than either high- or low-tint antimony oxide. Generally, antimony–silico complexes are less effective flame retardants than antimony trioxide. Therefore, although the cost per kilogram is less than antimony trioxide, the cost-effectiveness of the antimony–silico complexes can be higher.

Antimony–Halogen Mechanisms: Antimony trioxide is used almost exclusively with heat-labile halogen compounds. Most of the mechanisms proposed indicate that antimony trioxide is activated by reaction with halogenes, forming antimony trihalides or antimony oxyhalides. This can be shown simply by the following reactions:

Antimony trichloride and antimony oxychloride work primarily as flame-phase flame retarders. The type of antimony halide formed depends on the concentrations of the hydrogen halide and the temperature of the reaction.

In this study, a typical aliphatic chlorinated paraffin containing 70 wt % chlorine (Chlorowax, Diamond Shamrock) was heated alone at a rate of 20°C/min. A 67% weight loss was noted at 250–360°C (see Fig. 2). The loss is equivalent to 93 wt % of the theoretical stoichiometric quantity of hydrogen chloride.

When an equal weight of antimony trioxide was added to the chlorinated paraffin and the mixture was heated at the same rate, a 76% weight loss at 310–400°C was noted (see Fig. 3). If there were no reaction, the loss would have been only 37.5% since only half of the mixture was the chlorinated paraffin, and antimony trioxide does not volatilize below 656°C. The higher weight loss indicates that some reaction between either the decomposition products of the chlorinated paraffin or the chlorinated paraffin itself and antimony trioxide have taken place. The gas generated by the reaction has been analyzed and identified as antimony trichloride. The weight loss is equivalent to 90% of the theoretical quantity of antimony trichloride that can be formed from the mixture. From this thermal analysis, it is apparent that antimony trichloride is the predominate antimony species formed from combination of antimony trioxide and aliphatic chlorine compounds that generate high concentrations of hydrogen chloride upon thermal degradation.

It appears that antimony oxyhalides are the primary antimony compounds formed when organic halogen compounds, which do not generate hydrogen chloride directly upon thermal exposure, and antimony trioxide are heated together.

Antimony trihalides are the flame-retarding species whether they are generated directly from the starting antimony–halogen mixture or from antimony oxyhalide (18). They inhibit combustion by altering the manner and type of decomposition products formed by the plastic and by modifying the reactions in the flame to make them less exothermic. In the condensed phase or molten polymer just beneath the flame, antimony trihalide promotes reactions that form carbonaceous chars instead of highly volatile reactive gases. The chars act as heat shields, which deflect the heat of the flame, and slow down the thermal and oxidative decomposition of the polymer. The chars also form a seal around the polymer preventing potentially flammable gas from escaping and entering the flame.

Once in the flame, the antimony trihalides decomposes into various antimony oxides and halogen compounds. The decom-position mechanism has not been completely determined.

A decomposition mechanism has been proposed in which antimony trihalides such as antimony tribromide decompose in a stepwise manner and participate directly in flame-quenching reactions.

Boron Compounds

Approximately 2700 metric tons of borates was used as flame retarders for poly(vinyl chloride), cellulosics and unsaturated halogenated polyesters in 1979. Zinc borate is by far, the most widely used of
this class of compounds. There is a variety of zinc borates available that vary in zinc, boron and water content. Manufacturers and trade names of commercially available borate flame retardants are shown in Table 4.

Zinc borate is rarely used alone. It acts synergistically with antimony oxide, enabling compounders to extend antimony trioxide in some formulations. Zinc borate is also used with high levels of aluminium trihydrate in some halogenated unsaturated polyester resins.

Boric Acid-Sodium Borate: Boric acid [10043-53-3] and sodium borate [1303-94-4] (borax) are two of the oldest known flame retardants. They are used primarily to flame-retard cellulosics such as cotton (qv) and paper (qv). Both products are in expensive and fairly effective in these applications. Their use is limited to products for which nondurable flame retardancy is acceptable since both are very water soluble.

Boron Mechanism: Boron compounds function as flame retardants in both the flame and condensed phases. Flame-phase-active boron compounds are generated from combination of borates and halogenated organic compounds. These compounds usually generate boron trihalides, which have been used to reduce the flame volatility of air–hexane mixtures.

Boric acid and borax are effective condensed-phase flame retardants in polyhydroxyl compounds, especially in cellulosic fibers. When these compounds are exposed to a flame, they melt and form a glasslike coating around the fibers. Prolonged exposure causes the coating to dehydrate, generating water which cools the flame and cause it to extinguish. The boron residue also reacts with the hydroxyl groups of the cellulose to generate additional quantities of water and form an inorganic char that is difficult to ignite and burn. The char is an insulator that slows down the rate of polymer degradation and fuel formation.

Boron compounds that also contain other metals are active in both phases. Although zinc borate is not used alone to flame-retard PVC, it does inhibit flammability in the condensed and flame phases. Upon exposure to the flame, the PVC generates hydrogen chloride which can react with the zinc borate to form nonvolatile zinc compounds as well as volatile and nonvolatile boron compounds.

The nonvolatile zinc compounds and boric acid promote char, reducing fuel formation, and the boron trichloride and water cool and extinguish the flame.

Ammonium Fluoroborate: Ammonium fluoroborate [13826-83-0], NH₄BF₄, is another boron-containing compound that has some utility as a flame retardant. It can decompose to yield both halogen and boron functionalities to the flame-retarding process. Flame-retardant plastic formulations recently published suggest that ammonium fluoroborate should be used primarily in combination with antimony trioxide. Manufacturers propose that the following reaction describes functionally what takes place when the two products are exposed to flaming conditions.

The products formed contribute to extinguishing the flame by the mechanisms proposed in preceding paragraphs.

Principal producers of ammonium fluoroborate include Allied Chemical Corporation, Marcus Hook, Pa.; Cabot Corporation, Boyertown, Pa.; and Harshaw Chemical Company, Cleveland, Ohio.

Alumina Hydrates

Approximately 159, 000 metric tons of alumina trihydrate [21645-51-2] (ALTH) was used to flame-retard unsaturated polyesters and foam carpet backing in 1979. ALTH is made either from bauxite by the Bayer process or from recovered aluminium by the sinter process. Physical properties listed in Table 5 and principal suppliers in Table 6.

Aluminium trihydrate is the only aluminium compound of commercial significance as a flame retardant. It functions as a flame retardant in both the condensed and flame phases.

When aluminium trihydrate is exposed to temperature above 250°C, it forms water and alumina. The evolution of water absorbs heat. The water cools the flame and dilutes the flammable gases and
oxidant in the flame. The aluminium residue, an excellent heat conductor, increases removal of heat from
the flame zone.

Although ALTH is an inexpensive compound, it is a comparatively inefficient flame retardant. High
add-on level, up to four times as much as the plastic itself, are needed to impart acceptable flame
retardance. It is used alone only in polymers in which large amounts of filler can be tolerated and increased
weight (or density) is desired. The major application areas for ALTH are filled thermoet polyesters and
styrene–butadiene rubber latex rug backing.

Alumina trihydrate is also used as a secondary synergist to improve the flame retardance of polymer
systems that already contain antimony trioxide, zinc borate or some phosphorus flame retardants.

Molybdenum Oxides

Molybdenum compounds have been used as flame retardants of cellulosics for many years (see
Molybdenum compounds). Recently, they have found some use in other polymers. Molybdenum
compounds appear to function as condensed-phase flame retarders. After ignition of PVC formulations
containing molybdenum oxide [1313-29-7] (MoO3) and antimony oxide, 90% of the molybdenum remained
in the ash and only 10% of the antimony was found.

Since most of the molybdenum remained in the ash and the formulation did have flame-retardant
properties, molybdenum is probably a condensed-phase flame retardant that promotes char. The precise
mechanism of action has not been sufficiently defined to warrant further speculations.

Surfactants
Anionic Surfactants

Introduction

The hydrophilic moiety in anionic surfactants is a polar group that is negatively charged in aqueous
solutions or dispersions. In commercial products it is either a carboxylate, sulphonate, sulfate or phosphate
group. In dilute alkaline solutions in soft water the solubilizing power of the sodium salts of the four anionic
radicals is approximately equal and strong enough to balance the hydrophobic tendency of a 12-carbon
saturated hydrocarbon group; the sulfate is actually a somewhat stronger solubilizer than the sulphate. In
neutral or acidic media or in the presence of heavy-metal ions, the solubilizing power of the carboxylate is
markedly less than that of the other groups.

The ionic environment associated with anionic surfactants influences the properties of their solutions.
Sodium and potassium salts are generally more soluble in water and less soluble in hydrocarbons.
Conversely, the calcium, barium and magnesium salts are more compatible with hydrocarbon solvents and
less so with water. Ammonium and amine salts, e.g., triethanolamine, improve the compatibility of anionics
with water and hydrocarbons and are widely strengths are usually associated with lower solubilities of
anionic surfactants. To offset this effect, the molecular weight of the hydrophobe is lower in products
designed for use at high electrolyte affected by total-ionic strength and also by the identity of the associated
cations. The anionic surfactants can be divided into four groups according to their anionic groups—(1)
Carboxylates, (2) Sulfonates, (3) Sulfates and Sulfated Products, (4) Phosphate Esters.

Carboxylates

Soaps and a small volume of aminocarboxylates are the only commercial products in the carboxylate
class of surfactants. Two types of aminocarboxylate surfactants, N-acylsarcosinates and acylated protein
hydrolysates, are produced in small quantities as specialities. Both series of products are fatty acyl
derivatives of aminocarboxylates. As compared to the corresponding soaps, the hydrophilic tendency of the
amide linkages in these molecules is strong enough to significantly lessen inactivation of the carboxylate
ions by the calcium and magnesium ions that are present in hard water.

Soap
For many years soap was the only surfactant produced commercially. Inspite of the development of many new surfactant types, it may be noted that soap possesses some desirable properties which are not found in many other surfactants. The sodium and potassium cocofatty acid soaps are unexcelled as lathering and cleansing agents in bar detergents for personal use in soft to medium hard water. The C14 to C18 fatty acid sodium soaps are effective laundry and industrial detergents in soft to medium hard hot water. Soaps, especially amine salts, are excellent emulsifiers, dispersants and solubilizing agents with a wide range of industrial uses. Soaps have an emollient action in contact with the skin and leave a soft feel on textile fabrics.

**N-Acylsarcosinates**

Sodium N-lauroylsarcosinate and the N-acylsarcosinate derived from coconut fatty acids are soap like detergents with good lathering properties. They are principally used in dentifrices where it is claimed they also inactivate the enzymes that convert glucose to lactic acid in the mouth. N-Oleoyl-sarcosinate is used as a textile auxiliary and detergent. The N-acylsarcosinates are prepared by the condensation of a fatty acid chloride with sarcosine (i.e., N-methylglycine obtained from the reaction of methylamine, formaldehyde, and sodium cyanide) in alkaline aqueous solution.

**Acylated Protein Hydrolysates**

Fatty acyl aminocarboxylates are prepared from protein hydrolysates by acylation with fatty acid chlorides or by direct condensation with fatty acids. The commercial products are mixtures that vary in composition from acyl derivatives of polypeptides from incompletely hydrolyzed protein to mixtures of acylated amino acids derived from completely hydrolyzed protein. Collagen from leather scraps and low grade-hide glues is used as a source of protein. Derivatives of the incompletely hydrolyzed peptides have a great tolerance for hard water but their effectiveness as surfactants is lower.

**SULFONATES**

The most effective structure for an anionic surfactant is a sulfonate of the general formula RSO3Na where R is a biodegradable hydrocarbon group in the surfactant molecular weight range. The R group can be alkyl or alkylarylene and the product can be a random mixture of isomers as long as it does not contain chain-branching that interferes with biodegradability. The surface activity of the SO3– group is not oversensitive to variations in the pH or to heavy metal ions and the C–S linkage is not susceptible to hydrolysis or oxidation under normal conditions of use.

Sulfonation processes on surfactant raw materials can usually be adjusted to increase or decrease slightly the degree of substitution of the solubilizing group on the hydrophobe. The average molecular weight of the hydrophobic bases can also be increased or decreased slightly. Minor adjustments in these two variables produce significant differences in performance. Sulfonates are usually obtained in the production process as free acids that can be neutralized to form alkali metal salts, alkaline earth metal salts, or amine salts; thus neutralization is another parameter for modification of properties. Manipulation of these variables leads to products with a multiplicity of combinations of properties from the same raw materials and production equipment.

The surfactants of commercial importance in this group are alkylbenzene sulfonates, petroleum sulfonates, di-alkyl sulfosuccinates, naphthalene sulfonates, N-acyl-N-alkyltaurates, 2-sulfo ethyl esters of fatty acids and olefin sulfonates.

**Alkylbenzene Sulfonates**

Linear dodecylbenzene sulfonates rank next to soaps in total usage. The sodium salt of linear dodecylbenzene sulfonate is commonly referred to as ‘LAS’. Linear dodecylbenzene sulfonic acid is called LAS acid, and salts other than sodium are named in an analogous manner, e.g., LAS ammonium salt. Commercial dodecylbenzene sulfonic acid is a light coloured, viscous liquid that is used almost entirely as an intermediate for the manufacture of alkalimetal, alkaline earth metal, and amine salts.
In comparisons of the performance of alkylbenzene sulfonates to that of aliphatic sulfonates, the effect of the benzene ring is often considered as approximately equivalent to three carbon atoms in an aliphatic chain. Alkylbenzene sulfonic acids are strong organic acids and form essentially neutral alkalimetal salts that have a good solubility in aqueous solutions at use concentrations over the entire pH range. These acids are not sensitive to precipitation by the natural hardness of the surface waters, but the alkaline earth metal salts are less water soluble than the alkali metal and amine salts. The calcium salts are sufficiently soluble in hydrocarbons for use in these media. The alkylbenzene sulfonates are one of the most chemically stable types of surfactants. The sulfonic group is not susceptible to acidic or alkaline hydrolysis under normal conditions of storage or use. The compounds are stable to strong oxidizing agents in aqueous solutions at use concentrations and are stable in carefully formulated products containing oxidizing agents.

The surface activity of unformulated, unbuilt dodecylbenzene sulfonates is sufficiently strong for the salts to be useful for their detergente, wetting, emulsifying, dispersing, and foaming properties, but they are not outstanding surfactants. The widespread usage of LAS stems from other factors which include their low cost reproducible quality, adequate supply, light colour, low odour, and excellent response to formulation and builders. For example, LAS solutions are only average foamers but mixtures of LAS with foaming properties. Similarly, LAS performs well in built heavy-duty cleaning products where the wetting, foaming, emulsifying and dispersing properties of the surfactant component are as important as the detergency power. Amine salts of LAS & ABS acids are used in blends with other emulsifiers, particularly the non-ionic types, in emulsifiable concentrates of pesticides.

**Petroleum Sulfonates**

The petroleum sulfonates are the only large-volume class of surfactants that are used predominantly in non-aqueous systems. They are available as coproducts of the refining of certain petroleum fractions. They are usually grouped into two broad classes—water soluble types called ‘green soaps’; and oil soluble types called ‘mahogany soaps’ (which may also be soluble in water).

The green soaps are of little use. The mahogany soaps are valuable for their properties of solubilization, detergency, dispersion, emulsification, and corrosion inhibition. Their principal use is in lubricating oils for sludge dispersion, detergency, micellar solubilization of water, and corrosion inhibition. They are also widely used in other products for corrosion inhibition and emulsification. Alkylaromatic hydrocarbon sulfonates are the surfactant components in both product types. The green soaps contain a higher proportion of disulfonates than the mahogany sulfonates, which are principally monosulfonates.

**Dialkyl Sulfosuccinates**

Sodium di (2-ethyl-hexyl) sulfosuccinate is the largest volume product of this group. It is now a widely used specialty surfactant. These sulfosuccinates as sodium salts are available as white, waxy, odourless solids or as concentrated colourless solutions. The di–C8 esters have the optimum solubility balance for use in tap water or aqueous solution with low inorganic salt content; lower alkyl esters are more effective in saline solutions. Sodium dialkyl sulfosuccinates are highly surface active but the susceptibility of the ester linkage to acidic or alkaline hydrolysis limits their usefulness. The products have strong wetting, rewetting, penetration and solubilization properties. The symmetrical diesters are produced by esterification of maleic anhydride using conventional technology followed by addition of sodium bisulfite across the olefin linkage.

**Naphthalene Sulfonates**

Four series of specialty surfactants make up the widely used but relatively low-volume group naphthalene sulfonate products, viz., salts of alkynaphthalene sulfonates; salts of sulfonated formaldehyde-naphthalene condensates; salts of naphthalene sulfonates; and salts of tetrahydronaphthalene sulfonates.

In the concentrated dry form, most of the salts are almost odourless light-grey solids. They are readily and highly soluble in water. In fact, except for the nonyl derivatives, the naphthalene soft water. The
Naphthalene sulfonates are stable to hydrolysis in acidic or alkaline media and are not sensitive to oxidation by strong oxidizing agents under use conditions. The naphthalene sulfonates are used in many different applications as wetting and dispersing agents. Several members of the series are effective as stabilizing and suspending agents in disperse systems. Some of the products are useful for their solubilizing properties. Hard water does not adversely affect the surface activity of typical members of the series.

**N-acyl-N-alkyl-taurates**

The taurates are technically interesting as the only class of anionic surfactants with the combination of many advantages. They are stable against hydrolysis by acidic or alkaline media at use concentrations. They show no loss of performance in hard water. They have soap-like biodegradability and residual feel on washed fabrics; and they have a molecular structure capable of yielding either strong wetting or strong detergent configurations. For example, the products RCON(R¢)CH2CH2SO3Na are strong detergents when R = C11 – C17 and R¢ = CH3 or C2H5, but are strong wetters when R = R¢ = C6 – 9. Relatively high raw material costs have held usage of the presently available N-acyl-N-alkyl taurates in the specialty category and have precluded the introduction of additional products with markedly different properties. The commercial product N-Oleoyl-N-methyltaurate is marketed as a light-yellow solid at about 70 per cent assay or at lower concentrations in water as a light-coloured slurry, solution or gel. It is principally used in detergent applications without builders. Foaming of the N-methyl derivatives is only moderate and is not readily improved by the usual foam builders; the N-cyclohexyl derivatives are low foaming detergents with good wetting power.

The production of sodium N-oleoyl-N-methyltaurate involves three chemical steps and yields average 95 per cent or higher in each step.

**2-Sulfoethyl Esters of Fatty Acids**

These products, known commercially as b-sulfoesters, resemble closely in properties the fatty acids from which they are derived, but they have the advantage that hard water does not impair their performance. Only the sensitivity of the ester linkage to hydrolysis has prevented their widespread usage in consumer detergents. Hydrolysis is not a problem with detergents for personal use and the sodium salt of the 2-sulfoethyl ester of lauric acid, or similar coconut acid mixture, has found acceptance as the foaming and cleansing ingredient in synthetic detergent bars. The oleic acid analog is less foaming but is a good detergent with specialty uses in neutral or mildly alkaline systems.

The esters can be produced commercially from isethionate (obtained by the reaction of ethylene oxide with a concentrated solution of sodium bisulfite) and the fatty acid or acyl chloride. The reaction between the acyl chloride which is a viscous liquid and the powdered, anhydrous sodium isethionate is carried out in the absence of water or solvent under vacuum in a heavy duty mixer. After the total charge is added to the reactor and brought to temperature, HCL is rapidly evolved, leaving the finally divided, light coloured product as the sodium salt.