Introduction

1. Functional dyes

Textile dyeing and functional finishing both are necessary but traditional separated processes employed in textile treatment. Textile dyeing and finishing necessitate repeat wet treatments and drying, and thus consume large quantities of energy and produce large amounts of waste water [1-4]. Saving production costs by reduction energy consumption, production time, dyeing and finishing chemicals, and water, among other things, is an important goal of the textile industry. The industry is also consciously engaged in waste reduction and pollution prevention efforts [5]. Simultaneous dyeing and finishing in one bath could obviously reduce both energy and wastes. Recent work has demonstrated that the combination of these two processes is feasible.

However, the different treatment conditions required for textile dyeing and functional finishing generally limit the application of such processes to the mixing of colorants and finishing agents in a one step treatment. As an alternative approach, if a functional agent was chemically incorporated into dye without significantly affecting its dyeing properties, the textile dyeing and finishing could be unified into one process [14]. That,

- Does not compromise dyeing and / or finishing conditions.
- Does not sacrifice the properties of resultant textiles.
- More economically and eco-friendly.

The functional finishing dyes allow dyeing and functional finishing to be achieved simultaneously thereby reducing the amount of solvent used and the amount of waste solvent generated. Moreover simultaneous dyeing and functional finishing of textiles reduce the amount of labor and time required to produce such treated textiles.

These advantages result in the overall cost reduction in dyeing and treating textiles [6]. The design of a functional dye becomes the key to fulfill one process of textile dyeing and functional finishing.

Textile surfaces porous and surface areas typically are quite large, allowing prolific bacterial growth under favorable temperature and humidity conditions .pathogenic bacteria are the source of many human diseases. Antimicrobial finishing is an important step in textile finishing, particularly for textiles that will come in contact with children, doctors, nurses and soldiers. Textile finishing increases the utility of textiles, but requires more energy resources and uses greater amounts of water [7]. Producing functional dyes with special finishing capabilities currently is an area of active research [8].Many functional dyes, such as water–repellent dyes [9, 10], anti-UV radiation dyes [11-13], and antimicrobial anthraquinone dyes [14-17], have been reported.

In 1981 the term “functional dye” appeared for the first time in Japan. This new term has come out of renewed interest and activity in the field of dye chemistry with increasing needs for organic materials applicable to the advanced high technologies which had never been connected with traditional dye chemistry [18].

Functional finishing dye is a dye containing at least functional finishing group covalently attached to traditional dye via a chemical linkage[14] as Figure (1).

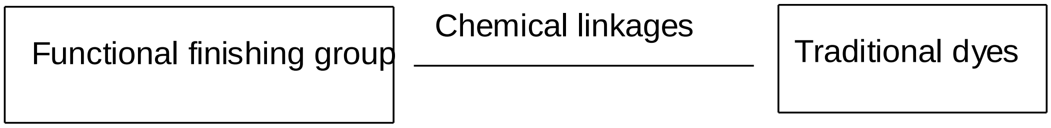


Figure (1.1): The structure of functional dyes

Functional dyes and colorants are compounds whose electronic structures can absorb electromagnetic radiation in visible range (380 -780 nm), additional properties other than color can be defined as a functions. Based on this definition, infrared dyes, laser dyes and voltage sensitive dyes fall within the category of functional dyes [14, 19].

Functional dyes and colorants are useful for imparting a functional property to a textile such as antimicrobial, anti - static , softening, water repellent, fire -resistant, soil – repellent, anti - UV, and a chemical properties as well as a combination of two or more properties thereof [6] .

1.1. Functional dyes can be used in the following fields [18]

1- Dyes for information recording media.

- Pressure-or heat sensitive dyes used as color formers in carbonless paper or facsimile recording system.
- Organic photoconductors in electro photography.
- Dyes for the diffusion thermal transfer system.
- Dyes for ink-jet printing.
- Infrared dyes for laser optical recording systems.
- leuco dyes for radical photography.

2- Dyes for information display media.

- Dhermo chromic, photo chromic and electro chromic dyes.
- Electro luminescence and indicator dyes.
- Dichoric dyes for gust-host liquid crystal display, polarized film and color filter system.

3- Dyes for energy – transfer and storage system.

- Dyes for solar batteries, light collectors and non linear optics.

4- Dyes for optical catalysts and photo resists.

5- Dyes for probes and indicators.

6- Dyes for medical and biological applications.

2. Antimicrobial dyes

The first question we must consider **what are microbes**? Microbes are the tiniest creatures not seen by the naked eye. They include a variety of micro-organisms like bacteria, fungi, algae and viruses. Bacteria are uni – cellular organisms which grow very rapidly under warmth and moisture. Further, subdivisions in the bacteria family are Gram positive (Staphlyococcus aureus), Gram negative (E-Coli), spore bearing or non spor bearing type. Some specific types of bacteria are pathogenic and cause cross infection. Fungi, molds or mildew are complex organisms with slow growth rate. They stain the fabric and deteriorate the performance properties of the fabrics .Fungi are active at a pH level of 6.5. Algae are typical micro organisms which are either fungal or bacterial. Algae require continuous sources of water and sun light to grow and develop darker stains on the fabrics. Algae are active in the pH range of 7.0-8.0. Dust mites are eight legged creatures and occupy the household textiles such as blankets bed linen, pillows, mattresses and carpets. The dust mites feeds on human skin cells and liberated waste products can cause allergic reaction and respiratory disorders [19].

Textile materials are excellent media for growing of microorganisms, an environmental concern, to the public, due to increasing cross transmission of diseases in hospitals and unhealthy indoor air quality in working areas partially or completely caused contaminated textiles .Body odor, and dermal infections caused by microorganisms, are hygienic concern as well.

Clothing and textile materials are carriers of microorganisms such as pathogenic bacteria, odor generating bacteria, and mold fungi, because of the adhesion of these microorganisms on fabric surfaces.

Most textile materials currently used in hospital and hotels are conductive to cross-infection or transmission of diseases caused by microorganisms. The spread of HIV and hepatitis viruses by contact of contaminated materials has created increased pressure for protection of personal with functional clothing and materials [20].

Antimicrobial dyes are dyes which have the ability to kill at least some types of microorganisms or to inhibit the growth or reproduction of these organisms [6].

Fabrics possessing inherent antimicrobial functions are expected to be able to completely eliminate these concerns [4]. Therefore, medical use and institutional use apparel materials and clothing such as surgeons' gowns, patient drapes, nurses' clothing, carpeting and bedding materials, lining sheets and towels, and worker uniforms are necessary to achieve antibacterial functions [21].

In the last few decades, the prevention of microbial attack on textile and wearers of textile materials has become increasingly important to consumers and textile producers [22], therefore, interests in antimicrobial fabric finishing have steadily increased over the last few years. The major classes of antimicrobial agent for textiles include organo–metallics, phenols, quaternary ammonium salts, and organo-silicones, to be successful in the market place, thus finishes should be durable and have selective activity towards undesirable organisms.Safety, non–toxicity and biodegradability are required for antimicrobial agents [23, 24].

Textiles dyed with antimicrobial dyes have microbiocidal (i.e. antimicrobial), activity against abroad spectrum of pathogenic microorganism e.g. gram-positive (staphylococcus aurous) and gram negative (Escherichia coil) bacteria. The microbiocidal properties of the textile can also be used for women's wear, under wear, sockes and other hygienic purposes such as upholsteries.

In addition, the microbiocidal properties can be imparted to carpeting materials to create odor-free and/or germ- free carpets, Moreover, all germ–free environments, such as those required in biotechnology and in the pharmaceutical industry, can benefit from the use of the microbiocidal property to prevent any contamination from air, liquid, and/or solid media [6].

3. Chemical finishes

Depending on different functional or performance needs, a number of chemical finishes is available on the market. Generally, they can be categorized into durable press finishes [25- 28], water and water repellant finishes [29, 30], soil release and stain release finishes [31], softeners [32, 33], shrink resist finishes for wool [34- 36], flame retardant finishes [37-39], antimicrobial finishes [40- 43] and so on.

3.1. Requirements for antimicrobial finishes [44]

In order to obtain maximum benefits out of finish, the following requirement should be satisfied.

- Durability to washing , dry cleaning , and hot pressing ;
- Selective activity to undesirable microorganism;
- Should not produce harmful effects to the manufacturer , user and the environment ;
- Should comply with the statutory requirements of regulating agencies;
- Compatibility with the chemical processes;

  An ideal antimicrobial agent for textiles would have the following basic requirements;
- Non –toxic;
- Non- allergic;
- Non- carcinogenic;
- Antistatic;
- Compatible with common textile;
- Easy of application;
- No deterioration of fabric quality;
- Resistant to body fluids;
- Resistant to disinfection/ sterilization;
- Should be colorless and
- Should be economical.

3.2. Necessity of antimicrobial finishes [20]

Antimicrobial treatment for textile materials is necessary to fulfill the following objectives:

- To avoid cross infection by pathogenic micro organisms;
- To control the infestation by microbes;
- To arrest metabolism in microbes in order to reduce the formation odour; and
- To safeguard the textile products from staining, discoloration and quality deterioration.

3.3. Types of antimicrobial finishes

3.3.1. Leaching type (conventional antimicrobial)

Diffuse from the garment to come in contact with the microbe:

- Product migrates off the garment, forming a sphere of activity, and any microbe coming into the sphere is destroyed.
- But in the course of time the strength decreases and thus it just hurts the microbe, giving them a chance to born a stronger strains by mutation.
- The microbe consumes the antimicrobial as it acts on them. The product is eventually used up by the bacteria and slowly loses its effectiveness.

3.3.2. Non- leaching type

Bound to the product, allowing control of the microbes:

- Product does not migrate off the garments and destroy the bacteria coming in contact with the surface for the garment.

- The microbes do not consume the antimicrobials, which destroy them by acting on the cell membrane.
- These products do not lose their effectiveness; the finishing will be permanent and will remain functional throughout the life of the fabric will withstand more than 40 laundry washes [45].

4. Antimicrobial agents

Several major classes of antimicrobials are used in synthetic fibers. Most antibacterial, antifungal and broad spectrum antimicrobial agents have been investigated for their ability to impart microbiocidal and microbiostatic activity to the textile products.

4.1 Chlorinated phenols

The chlorinated phenolic compound triclosan is either incorporated into the polymer prior to extrusion and processing into fibers, or applied as topical finish .Triclosan emerges onto the surface of the fibers overtime and brings about biostatic or biocidial effects depending on the particular organisms or circumstances [46].

4.2. Silyquaternary compounds

Silyquaternary compounds have been popular as topical treatments for synthetic fibers for about two decades. Quaternary ammonium siloxanes bind by adhesive or chemical means, depending on the fiber substrate. Since they are not consumed by their interaction with the microbes, their activity can endure for the lifetime of the fabric, refreshed repeatedly by laundering [47].

4.3. Tolysulfone compounds

Tolysulfone compounds developed for some of the same applications targeted by the siloxanes and the broader spectrum biocidal biguardes, are now being used as topical fabric finishes [48].

4.4. Inorganic compounds

Inorganic antimicrobial agents, particular silver, have been successfully incorporated into synthetic fibers, especially for odor control, for a number of years, recently, there has been an explosion of interest in their use, along with a creative expansion of the forms in which they can be deployed, so they can best be considered as part of the range of emerging antimicrobial technologies.

4.4.1. Silver zeolite complexes

Silver particles in the form of silver zeolite complexes or metallic silver can be incorporated into synthetic polymer increasingly in the form of nanoparticles. Silver expression of the fiber surface takes place with diffusion from the body of the polymer, and the formation of silver ions in the presence of moisture, often as a result of dissociation from the stabilizing complexes to which the metal is bound. Moisture is necessary element for biocidal function, serving as a release inducer for the biocide at the fiber surface. Silver release rates can be influenced by the chemistry of the complexes used in fiber and gradual release can lead to extended biocidal activity.

4.4.2. Silver- polyhexamethylbiguanide complexes

Silver complexes with polyhexamethylbiguanide can be incorporated into polymers or fibers offering dual effect of the cationic polymeric biguanide and the silver released onto the surfaces [49] .

4.4.3. Zn-silver, zeolite complexes

Zinc is another heavy metal with effects on intercellular transport mechanisms, can be complexed with silver and zeolites so as to confer adualtype antimicrobial function as synthetic fibers including , those made by melt extrusion .

4.4.4. Silver – zirconium salts

Silver impregnation, some in the form of silver–zirconium salts, are becoming popular in nonwoven fabric used for wound dressings, because they confer a safe and reasonably broad spectrum antibacterial, enhancing wound healing.

4.5. Organic compounds

Several novel organic chemical technologies have come to light in the last few years that have relevance to the preparation of antimicrobial synthetic fibers. They bring modes of action and means of preparation to the field that are unique and exciting, opening up prospects for true contact biocide activity, with no diffusion and leaching of actives onto the fiber surface [47].

4.5.1. Polyvinyl pyridines

N- alkylated polyvinyl pyridines have been successfully bonded to range of inert surfaces so as to confer a durable antimicrobial function [47].

4.5.2. Diammonium rings

Diammonium ring compounds can be covalently linked to alkyl chains to generate a novel class of chemicals that bind to a varity of surfaces.

4.5.3. Photosensitizing compounds

Integration of photosensitizing compounds into polymeric coating has been shown to result in antimicrobial efficacy at surfaces subsequently exposed to visible light. Probably as a result of singlet oxygen and other free radicals generated by the photo-activated agent.

4.5.4. Quaternary ammonium compounds

Quaternary ammonium compounds, of many registered disinfectant and antiseptic formulation have been successfully bonded to synthetic fiber through the use of dye linkages [50, 51].

4.5.5. Chitosan

Chitosan-or more properly chitosans, since the polymers are generally heterogeneous population representing varying degree of chitin decetylation are increasingly used to confer antimicrobial properties on synthetic fiber as a topical finish. chitosan can be used to coat synthetic fibers in incontinence diaper cores as an odor control measure [52].

4.5.6. N-Halamine compounds

There has been a series of recent developments, in the applicability of N –halamine chemistry to the creation of durable, rechargeable synthetic fabrics with powerful antimicrobial properties, based on surface – bound chlorine.

5. The combination of dyeing and finishing

As mentioned earlier, simultaneous dyeing and finishing offer economical and environmental advantages in this field, such as the simultaneous dyeing and durable press finishing of cotton [53-55], the combination of dyeing and durable press finishing of silk [56, 57] as well as the simultaneous dyeing and finishing of wool [58].However, most of the studies are focusing on the treatment of natural fabrics, little study has been done in the area of synthetic fabrics. Furthermore, all of the reported study are concerning about the dyeing and durable press finishing, the combination of dyeing and other functional finishing is less developed. In addition, most of the single–step studies are designed for some specific systems. In these processes, the combination is usually based on the simple mixing of dyes, finishing and other auxiliaries, thus the compromise of dyeing and finishing conditions is usually required and the properties of the resultant fabrics are usually sacrificed. Therefore, further studies in the simultaneous dyeing and finishing are definitely needed.

In our study, functional dyes are proposed to combine dyeing and finishing together. In this approach, we hope to chemically link dyes and finishes into one structure, thus to achieve single – step dyeing and finishing by simply following the treatment conditions of certain dyes.

6. Cationic (Basic) Dyes

6.1. Historical and General

Mauveine, the first synthetic dye, was discovered in 1856 and was a basic dye. In common with many of its successors, it was notable for its brilliance of shade, high tinctorial strength, water solubility and poor fastness properties. It was this sheer brilliance which helped to spur the growth of the embryonic synthetic dye industry and within a generation most of the dull (drab) natural dyes known for millennia had been swept aside by the new synthetic or aniline dyes.

To get a qualitative idea of how this mordant dyeing process works, it is only necessary to appreciate that basic dyes are salts (like acid dyes) and dissociate in water to give anions and cations. In basic dyes (unlike acid dyes) the colored part of the salt is the cation (+) which is why they are frequently referred to as cationic dyes. The associated anion (-) can be something as simple as a chloride ion. Thus solid basic dyes can be represented by a general formula: Dye^+X^-, where X^- can be any of a number of relatively simple colorless anions.

In water the salt dissociates into colored Dye^+ cations and the equivalent number of anions. It is very rare for these colored basic dye cations to have more than one positive charge. This contrasts with acid dye anions which can have as many as four or more negative charges.

Despite their wonderful colors, the poor light fastness of many of the early synthetic or aniline dyes gave a bad name to synthetic dyes in general. The poor performers were notably the basic dyes and the acid dyes for wool derived from the same chromophores. This ill repute has proved hard to outlive despite the fact that there are many synthetic dye products which give dyeing of fastness properties impossible to achieve with natural dyes. If you don't believe it, all you have to do is visit an Oriental rug merchant. The first thing he will tell you about a carpet or rug is that it is dyed with natural dyes not aniline dyes. This backhanded slur on synthetic dyes can no longer be justified but has become a part of oriental carpet lore. With experience, a glance at the brightness and uniformity of orange or green areas in such carpets might give contrary indications because there are no true natural green or bright orange dyes. Through the early decades of the 20th century the end-use performance of synthetic dyes gradually improved, notably with the introduction of more and more anthraquinonoid (nonindigoid) vat dyes. But the retrieval of the poor reputation of the brilliant dyes and their chromophores had to wait another 50 years, until after the introduction of suitably modified polyacrylonitrile fibers [59] .

6.2. Chemical Nature of cationic (Basic) Dyes [60]

This class owes its name to the fact that the dyes ionize with the coloured component constituting the cation for this reason they are commonly referred to as cationic dyes. The general formula **Fig. (1.2):**

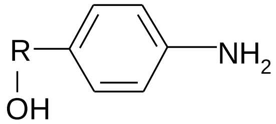
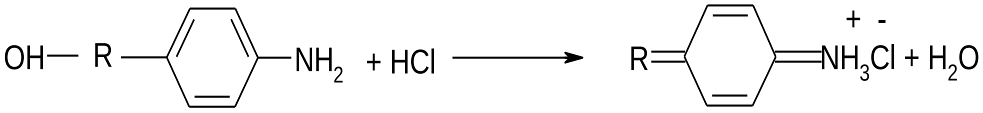


Fig. (1.2): General formula

Which is capable of salt formation as shown (Scheme 1)



Scheme 1

The base, containing no quinonoid chromophore, is colourless and the colour only appears on salt formation. Cationic dyes as they appear on the market are salts, usually the chlorides but sometimes the oxalate or even double salts with zinc chloride.

6.3. Classification of Basic Dyes

There are many dyes belonging to this class and they vary considerably in their chemical structure.

6.3.1. GROUP 1

These are derivatives of diphenylmethane. Since the chromophore is the C = NH group, they are known as the ketone imines. C.I. Basic Yellow 1 has the structure **Fig.(1.3)** and the colour is due to resonance with **Fig.(1.4)**:

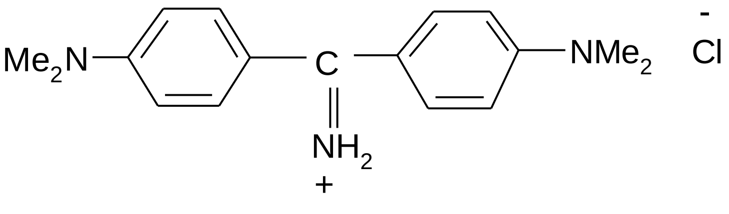


Fig. (1.3): C.I. Basic Yellow 1

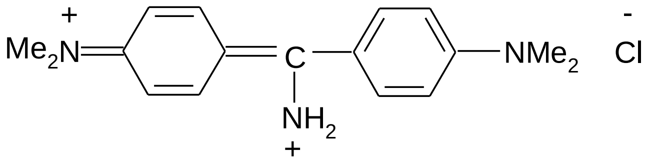


Fig. (1.4): Resonance C.I. Basic Yellow 1

6.3.2. GROUP 2 (Derivatives of triphenylmethane)

The following derivatives of triphenylmethane are of historical interest although they are no longer used **Fig. (1.5)**:

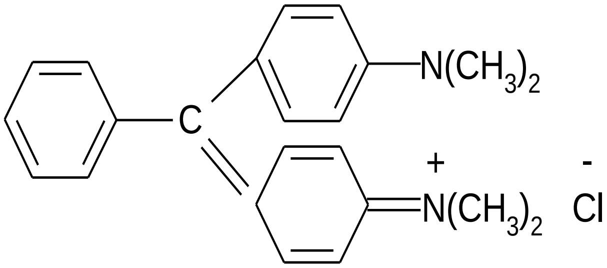


Fig. (1.5): Malachite Green C.I. Basic Green 4

6.3.3. GROUP 3

The thiazine dyes are based on the structure skeleton **Fig. (1.6)**

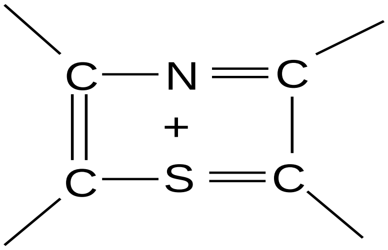


Fig. (1.6): Thiazine dyes structure

A well-Known example is Methylene Blue C.I. Blue 9 **Fig.(1.7):**

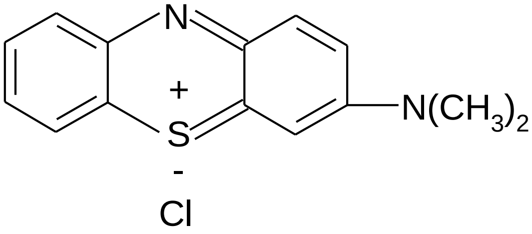


Fig.(1.7): C.I. Basic Blue 9

6.3.4. GROUP 4

The oxazine group resembles the thiazine with the exception that the sulphur atom is replaced by oxygen. Examples of historical significance are Meldola Blue (C.I. Basic Blue 6) **Fig. (1.8)**

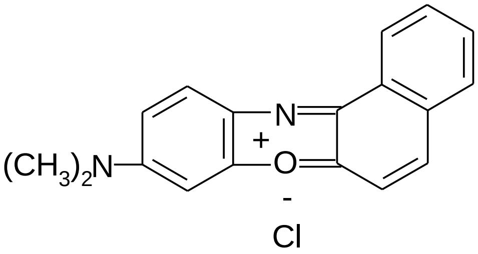


Fig.(1.8): C.I. Basic Blue 6

6.3.5. GROUP 5

The azines are based on the structural unit **Fig. (1.9):**

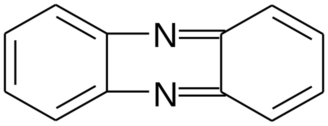


Fig. (1.9): The azines structural unit

They are of special historical interest because Perkin's Mauve **Fig. (1.10)** belonged to this group.

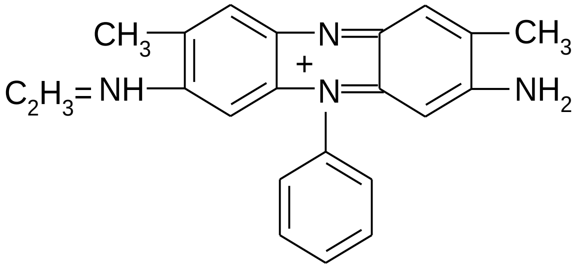


Fig.(1.10): Perkin's Mauve

6.3.6. GROUP 6

The xanthenes basic dyes are derived from the parent substance xanthene,Fig.(1.11) and a very well-known example is Rhodamine B (C.I. Basic Violet 10)**Fig.(1.12):**

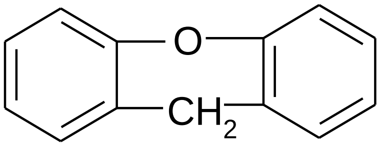


Fig.(1.11): The xanthenes basic dyes

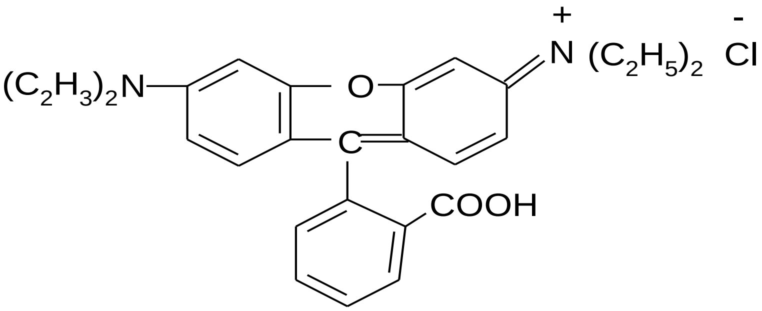


Fig.(1.12): Rhodamine B (C.I. Basic Violet 10)

6.3.7. GROUP 7

A number of basic dyes are substitution products of acridine **Fig. (1.13)** of which one example is Acridine Orange (C.I. Basic Orange 14) **Fig. (1.14):**

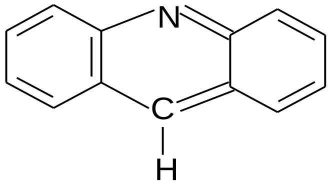


Fig.(1.13): Acridine

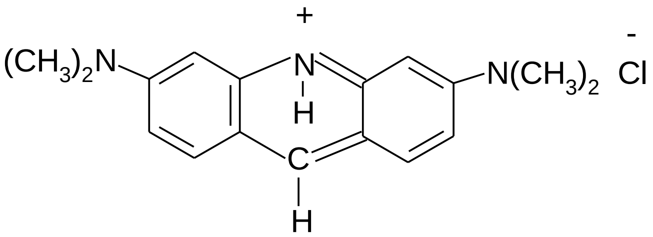


Fig.(1.14) : Acridine Orange (C.I. Basic Orange 14)

6.3.8. GROUP 8

These are basic dyes which contain azo groups such as Bismark Brown (C.I. Basic Brown 1) **Fig. (1.15):**

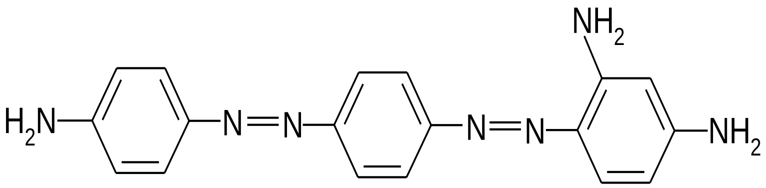


Fig. (1.15) : Bismarck Brown (C.I. Basic Brown 1)

The cationic dyes, mainly on account of their poor light-fastness, had virtually fallen into disuse until interest in them was revived when it was found that they were substantive to polyacrylonitriles, and possessed much better light-fastness on such fibres.

Although the fastness of the classical basic dyes was very much better with acrylic than with the traditional natural or regenerated fibres, nevertheless further improvements were called for. This lead to the introduction of new cationic dyes specifically intended for acrylics.

These fall essentially into three classes:

(1) Dyes containing a pendant cationic with a non-resonating charge such as **Fig. (1.16)**

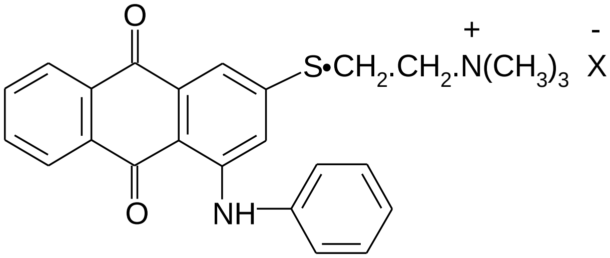


Fig.(1.16): C.I. Basic Blue 49

(2) Dyes with a delocalized charge such as **Fig. (1.17):**

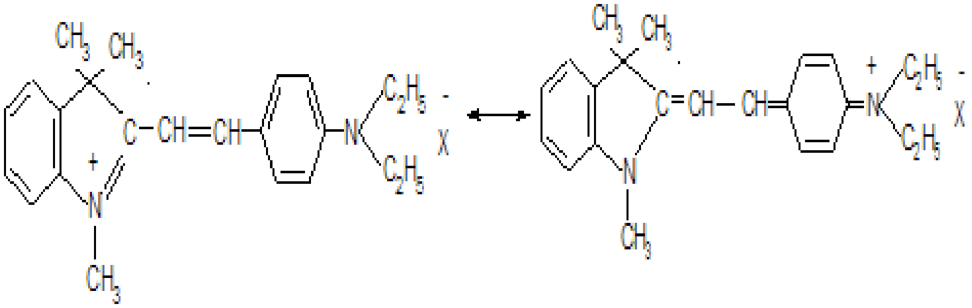


Fig 18:C.I.Basic Violet 7

(3) Dyes with a heterocyclic ring containing a quaternary nitrogen atom which does not form an integral part of the chromogen[60]. An example would be as shown in **Fig. (1.18)**.

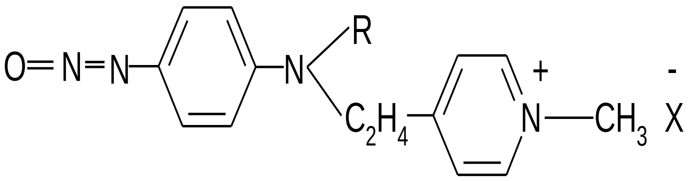


Fig.(1.18) : Dyes with a heterocyclic ring containing a quaternary nitrogen atom

6.4. Chemistry and General

The American Association Textile Chemist and Colorists (AATCC) Buyer's Guide [61] shows that basic dyes hold an important place in the textile dye market. There are 400 products listed under 85 C.I. Names, 42 of which also have published structures and C.I. Numbers. Of these, 31% are blues, 22% are reds and 22% are yellows. There are also oranges, violets and greens. Of the 85, almost half, 32 are offered as liquids.

There is no doubt that as group basic dyes are the brightest of dyes and their color gamut is enormous. Several are also highly fluorescent.

Although there is no real difficulty in dissolving basic dyes, which are usually pasted with glacial acetic acid followed by hot water and then sieved before adding to the dyebath, they are often sold as liquids. This is for convenience but also because the dust is so extremely highly colored and organic cationic materials are undesirable if inhaled.

The most interesting chemical feature of basic dyes is the variety of their chromophores, some of which are shown in **Fig. (1.19-1.24)**. They include anthraquinonoid, azo, oxazine, thiazine, xanthene and triphenylmethane. Many of the more traditional basic dyes have been known for a hundred years and more [61].

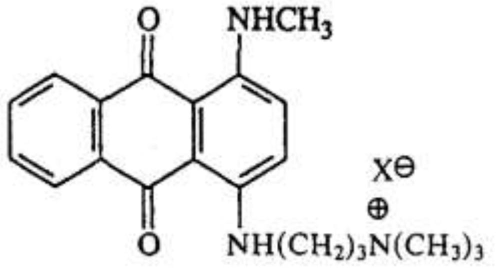


Fig.(1.19): AQ; e.g., C.I. Basic Blue 22.

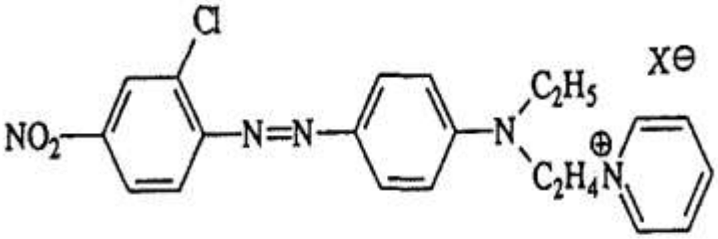


Fig.(1.20): Azo; e.g., C.I. Basic Red 18 type.

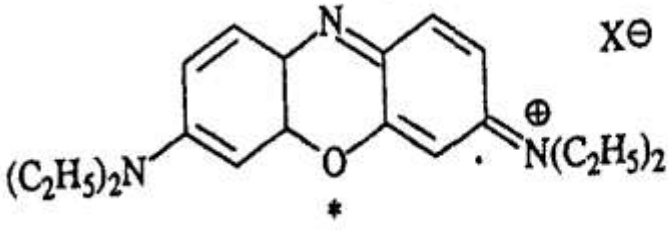


Fig.(1.21): Oxazines; e. g., C.I. Basic Blue 3

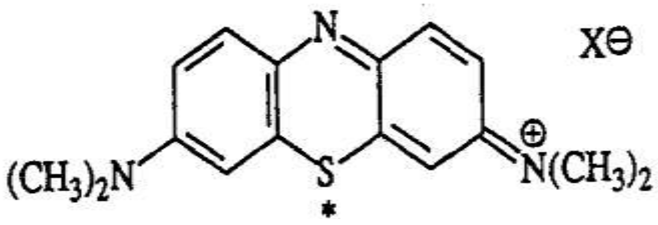


Fig.(1.22) : Thiazines; e. g., C.I. Basic Blue 9

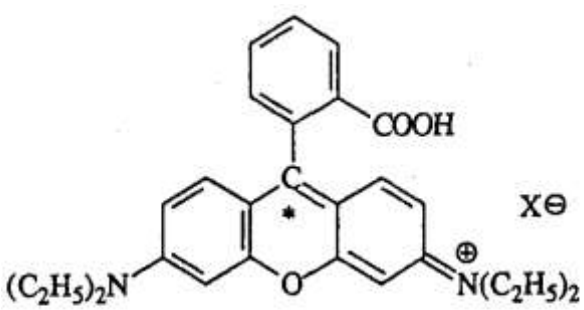


Fig.(1.23) : Xanthenes; e.g., C.I. Basic Violet 10.

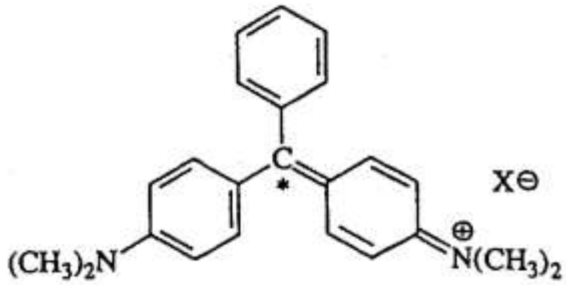
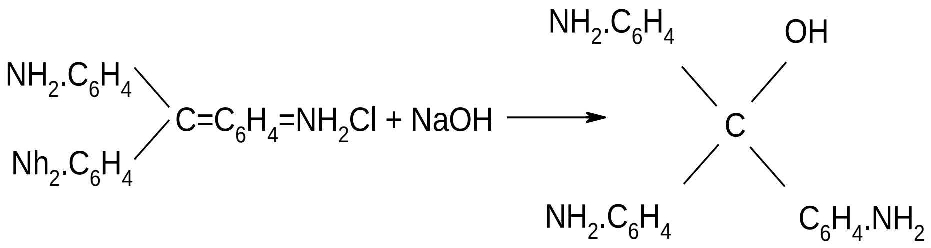


Fig.(1.24): Triphenylmethanes, TPM; e.g., C.I.Basic Green 4

6.5. Properties of Basic Dyes

The outstanding characteristic of the basic dyes is the brilliance and intensity of their colours: Some of the shades are of such clarity of hue that no other class can compare with them. The intensity is illustrated by a comparison of the dyeing properties of Magenta, which is a basic dye, and acid Magenta which has the same molecular structured but has been converted into an acid dye by sulphonation. Whilst 5 percent of the latter is required to produce a full shade on wool, only 2 to 3 percent of basic magenta is necessary. The basic dyes are readily soluble in alcohol or methylated spirit. They are not, as a rule, so easily dissolved in water and, unless care taken when dissolving them, they are liable to form a sticky mass which can be very difficult to bring into solution. Some of them, such as Auramine (C.I. Basic Yellow 2), are decomposed by boiling water and must be applied at temperatures of 60° to 65°C. Even the more stable ones tend to undergo slight decomposition with flattening of the shade on prolonged boiling. When a basic dye is treated with an alkali it is decomposed with the liberation of the dye base which is colourless (Scheme2).



Pararosaniline

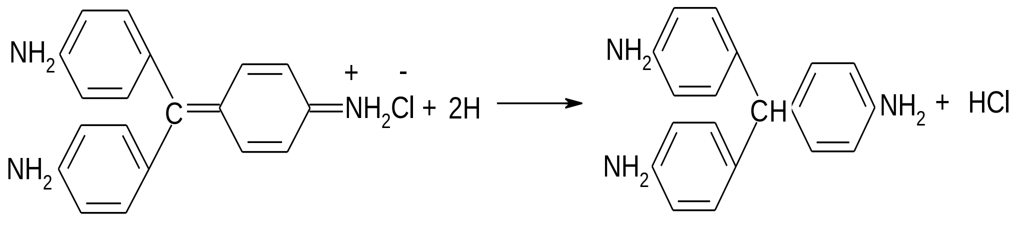
Scheme 2

Many of the dye bases are sparingly soluble in water. Thus, if sodium hydroxide is added to a solution of Methylene Blue, and the mixture allowed standing for some time, a flocculent precipitate of the base will appear. Water containing alkali or temporary hardness should therefore not be used with basic dyes without neutralizing first with acetic acid .Softened water generally contains sodium carbonate or calcium hydroxide and should be neutralized. The dye bases are soluble in ether and can be isolated by shaking a solution from which they have been precipitated with the solvent in a separating funnel.

Basic dyes, being cationic, can under certain conditions be precipitated by direct or acid dyes which are anionic. Consequently the two cannot be used together except at very low concentrations. Advantage can be taken of this mutual precipitation because the direct dye acts as a mordant when on dyed cellulosic materials, and therefore basic dyes can be used for after-treatment to brighten shades. The basic dyes are of poor fastness to light and vary with regard to washing fastness from poor to moderate.

An important property of basic dyes is that they will combine with tannic acid to form an insoluble product, provided mineral acid is absent. A precipitate is formed when a solution containing tannic acid, , in the presence of sodium acetate to neutralize mineral acid, is added to the dye Tannic acid has been used as a mordant for cellulosic fibres, and after-treatment with tannic acid and tartar emetic increases the wet-fastness of cationic dyes.

When treated with reducing agents most basic dyes are converted to colourless compounds with comparative ease, as is illustrated in the case of Pararosaniline scheme (3):



Scheme 3

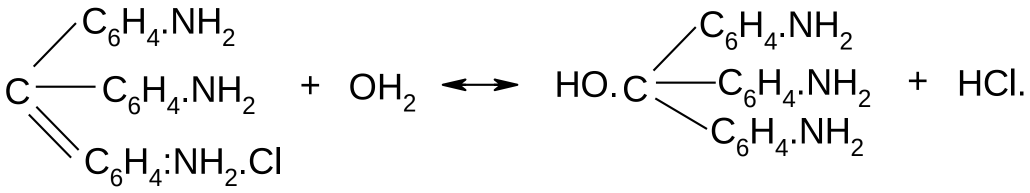
The product of reduction is usually very easily reoxidized to the dye, often even on exposure to air. An exception, however, is when the basic dye contains an azo group. The reducing agent then breaks the molecule down, at the azo linkage, into two components which cannot be reunited in their original form by oxidation [60] .

6.6. Use of cationic (Basic) Dyestuffs

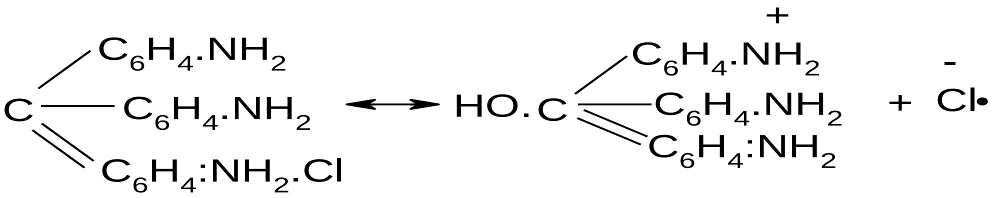
The basic dyes are used for dyeing knitting woollen yarns when particularly bright shades are required, which could not be obtained with an acid dye. Silk is very largely dyed with basic dyes. This fibre is used for fancy goods or dress materials where brightness of shade is of much greater importance than fastness to washing or even to light. A dyer never uses basic dyes on cotton if it can be avoided, since their use involves the troublesome process of mordanting with tannic acid. But, sometimes, bright shades are demanded, which can only be obtained with them. Rayons are often dyed with the basic dyes, nitro rayon having a direct affinity for them. They are used also for many purposes as making inks, typewriter ribbons, and dyeing leather [62].

6.7. Theory of Dyeing with Basic Dyestuffs

The view is generally held that dyeing with these dyestuffs is chiefly a chemical process, depending either upon hydrolytic or electrolytic dissociation of the dyestuff in the bath, followed by chemical reaction with the wool fibre, resulting in the formation of a colour lake. These two forms of dissociation may, in the case of para-rosaniline, be represented by the Scheme (4, 5):



Scheme 4



Scheme 5

According to the chemical theory, the liberated base or basic ion combines with the carboxyl groups of the keratin or fibron, hydrochloric acid remaining in the dye-bath or being adsorbed by the wool or silk.

It is an interesting fact observed by the authors that de-amination increases the affinity for methylene blue. The quantities taken up in each case were estimated by titration. It is possible that treatment with nitrous acid increases the numbers of carboxyl groups by converting amides into acids, thus Scheme (6):

$$R.CO.NH_2 + HONO = R.CO.OH + N_2 + H_2O$$

Scheme 6

Thorpe explained the dyeing of wool in the case of quinonoid dyestuffs by the fact that they readily form dissociated salts of the quinone-imine type, which are absorbed by the wool, leaving the acid in the bath [62], thus Scheme (7).

$$=C_6H_4{:}NH.HCl \longrightarrow =C_6H_4{:}NH + HCl.$$

Scheme 7

6.8. Nature of Substantivity

With very few exceptions, cellulosic fibres are not substantive towards cationic dyes.

With protein and most acrylic fibres there is good substantivity and there is good evidence that a salt linkage is formed [60]:

$$\text{Wool COO} \quad + \quad \text{Dye cation} = \text{Wool. COO (Dye cation)}$$

$$\text{A.SO}_4 \quad + \quad \text{Dye cation} = \text{A.SO}_4 \text{ (Dye cation)}$$

A = Acrylic substrate

6.9. Dissolving Basic Dyes

Owing to the relative insolubility and tendency to tar, special precautions are necessary when dissolving basic dyes. The dyestuff is first made into a paste with about its own weight of 30 percent acetic acid. Sufficient boiling water is then added with constant stirring to dissolve the dye, bearing in mind that the temperature of the water must not exceed 60°C with Auramine. It is sometimes advantageous to use methylated spirit instead of acetic acid to assist in preparing a satisfactory solution. The synthetic surface-active products used must be non-ionic or possibly cationic, because those which are anionic will precipitate the dye [60].

6.10. Assistants

The basic dyes have such a great affinity for the protein fibres that the presence of a retarding agent is often desirable. From 1 to 2 percent of acetic acid on the weight of goods is most frequently used for the purpose. The excess of hydrogen ions in the liquor, counteracts the attraction of the electronegative sites in the fibre and slows down the rate of adsorption of the dye ions. When acid has been used, the addition of small amount of alkali may be necessary towards the end of the dyeing to complete exhaustion. Since basic dyes are adsorbed in a neutral or alkaline bath, soap may be used as an assistant instead of acetic acid; from 10 to 15 percent on the weight of the goods is required when dyeing with soap, soft water is essential [60].

6.11. Application of Basic Dyes to Silk

The uses to which this fibre is put often call for the clarity and brightness of colour associated with the classical basic dyes. It probably was, and still is, their main textile application. The dye bath is made up with 0.5 kg per 1000 liters of acetic acid and the goods are entered cold. The temperature is raised to 80°C and it is advisable to add the dissolved dye in at least three portions whilst the temperature is being brought up.

The wet-fastness is improved by working the goods in a bath containing 1 percent of their weight of tannic acid for 20 minutes at 60°C or, alternatively, leaving them in a cold bath overnight. After squeezing, the load is transferred to a cold or lukewarm liquor containing a quantity of tartaremetic, $2(K\ (SbO).C_4H_4O_6)\ H_2O$, equal to half the weight of the tannic acid [60].

6.12. Application of Basic Dyes to Wool

Dyes of this class are now very rarely applied to wool but a few of the sulphonated triphenylmethane products, which are in fact acid dyes, find some applications. They require 1 to 3 percent w/w of acetic acid, and the liquor is brought to the boil slowly and retained at this temperature for 1/2 to 3/4 hour.

Many of these dyes are fast to sulphur dioxide and the colour can be brightened greatly by stoving. It is usual to bleach with peroxide before dyeing [60].

6.13. Application of Basic Dyes to Cellulose

Cellulose has, for all practical purposes, no substantivity towards basic dyes. In the past, cotton was mordanted with tannic acid and tartar emetic to achieve a degree of fixation [60].

6.14. Application of Basic Dyes to Acrylic Fabric

Basic dye is by far the most important class of dye used on acrylic fibre. Basic dyes dissociate in water to yield colored cations and are characterized by their brilliance and very high tinctorial strength. This dye class, which includes some of the earliest synthetic dyes, was originally used for dyeing wool, silk, and mordanted cotton, but the generally poor light fastness of the dyeing suppressed their use until the introduction of acrylic fibres on which the dyes exhibited higher light fastness and very good fastness to wet treatments [63].

7. Acrylic Fibers

7.1. Historical and General

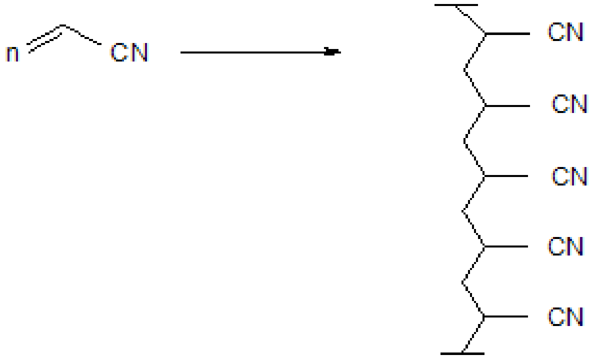
Polyacrylonitrile, or acrylic fibres as they are known, are prepared by addition polymerization of Acrylonitrile [63, 64] (scheme 8). The pure homopolymer is difficult to dye but acrylic polymers containing small amount of anionic centers, such as sulphonic acid or carboxylic acid groups, can be dyed readly with dyes bearing a positive charge, viz. cationic dyes. The cationic dyes are attracted to and then anchored to the fibre by ionic bonds (scheme 9). The anionic centers arise either from the polymerization inhibitors or from small amount of copolymer added deliberately to introduce the anionic sites.

Table (1.1) lists the major brands of polyacrylonitrile fibres and the anionic centers present.

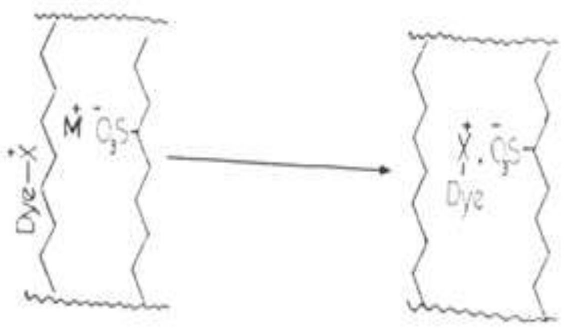
Acrylic fibres have important position in the textile industry and, there is always a continuous increase in the production and consumption of these fibres.

Table (1.1): Major Types of Polyacrylonitrile Fibres [63]

Orlon Dralon (Bayer) Acrilan (Chemstrand)	SO_3H groups
Courtelle (Courtaulds)	CO_2H groups



Scheme 8



Scheme 9

Acrylic fibres is defined as a fibre manufactured in which the forming substance is any long chain synthetic polymer composed of at least 85% by weight of acrylonitrile units[65]. A modacrylic fiber is defined as one composed of less than 85% but at least 35% by weight of acrylonitrile units [66].

Acrylic fibre is very different from other synthetic polymer fibre they also differ more among themselves due to the variation in the monomer used, monomer percentages to each other and polymerization technique [67].

Several polymers had been derived from the acrylonitrile monomers, $CH_2 = CH - CN$, as early as 1930. The reaction is called addition polymerization and involves the vinyl (or substituted vinyl) groups, $CH_2 = C<$, present in the monomers [68].

The structure of various comonomers is given in Table (1.2). The consequent structural disruption and loosening of the fibre-fibre bonds made for easier dye diffusion and also made the polymer easier to dissolve in suitable solvents. The further addition of comonomers from aliphatic and aromatic (benzenoid) vinyl sulfonates, such as methallyl and styrene sulfonates (Table 1.2), ensured that the fibres would be permanently anionic and bear negative charges; i.e., SO_3^- except at extremely low pH's. The negative charges underwrite the electrostatic (or coulombic) attraction of the fibres for the colored basic dye cations and for colorless cations as well [68, 69].

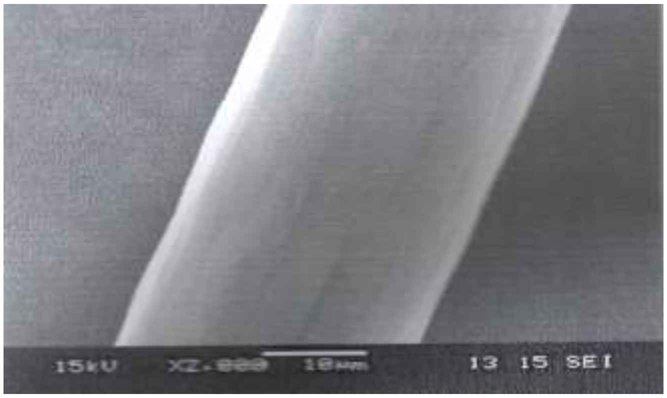


Fig.(1.25): Scanning electron microscopy (SEM) images showing the surface morphologies of Polyacrylonitrile [70].

Table (1.2): Some Substituents in Acrylic and Modacrylic Fibre Co monomers [71]

Co monomer Name and Nature	CH2=C(R1)-R2 Substituents	
	R1	R2
Neutral		
Methyl Acrylate	-H	-CO-O-CH3
Methyl Methacrylate	-CH3	-CO-O-CH3
Vinyl Acetate	-H	-O-CO-CH3
Anionic		
Allyl Sulfonate	-H	-CH2-SO3^{-}
Methallyl Sulfonate	-CH3	- CH2-SO3^{-}
Styrene Sulfonate	-H	-C6HSO3^{-}
Itaconic Acid	-COOH	-CH2-COOH
Neutral (FR Properties)		
Vinyl Chloride/Bromide	-H	-Cl/Br
Vinylidene Chloride	-Cl	-Cl

Modacrylic fibres are acrylic fibres which have included more than 15% but less than 65% of alternative comonomers to achieve particular properties such as improved flame retardancy. The additional comonomers are normally vinyl chloride or vinylidene chloride, Table (1.2), and for the optimal effect they should be present as 30 to 60% of total monomer. In fact, they could be present at higher concentrations than the acrylonitrile.

7.2. Manufacture of Acrylic Fibres

7.2.1. Acrylonitrile Properties

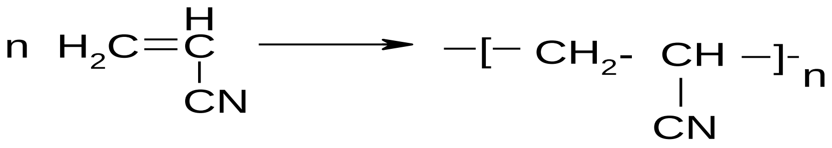
Acrylonitrile is the chief raw material for the acrylic fibres. It is a colourless liquid, easily handled in most of the standard unit processes. It is capable of rapid auto polymerization; molecular oxygen is an effective inhibitor so that there are no extraordinary storage problems. It is completely miscible with many organic solvents and appreciably soluble in water. The main steps are polymerizing the acrylonitrile, dissolving the polymer, spinning and after treating [66].

7.2.2. Polymerization

The polymerization of acrylonitrile is carried out by suspension, emulsion, and solution or bulk polymerization [72- 79].

7.3. Chemical Composition

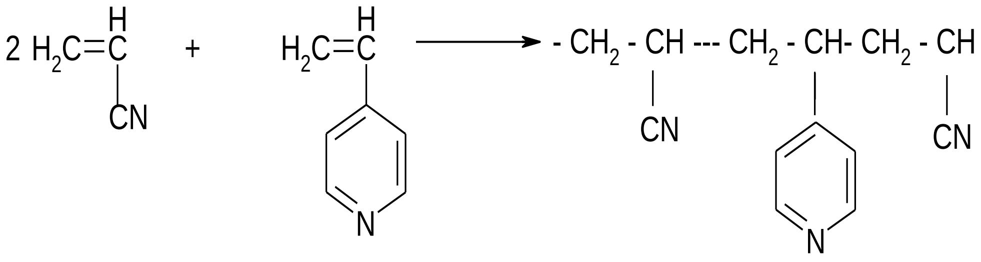
Acrylic fibres are mainly composed of Polyacrylonitrile which is prepared by polymerization of acrylonitrile molecules (scheme 10) [64]**.**



$$n\ H_2C{=}\overset{H}{\underset{CN}{C}} \longrightarrow -[-CH_2-\underset{CN}{CH}-]-_n$$

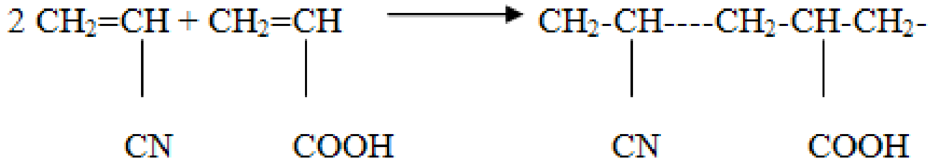
Scheme 10

The term "Acrylic fibres" refers to those fibres which contain more than 85% acrylonitrile unites, (CH2=CH- CN). Most acrylic fibres are made from copolymers including one or more monomers in addition to Acrylonitrile [80]**.** Such monomers are some ethylene derivatives, vinyl acetate, methacrylate, styrene, acrylamide, 2-vinyl pyridine, 2-methyl-5-vinyl pyridine, acrylic acid, methacrylic acid, or itaconic acid [64]. The common comonomers having affinity for acid dyestuffs are vinyl pyridine and methyl vinyl pyridine (Scheme 11). The ratio of these comonomers in polyacrylonitrile ranges from 2 to 5 % [81] .



Scheme 11

There are other comonomers which have affinity for cationic dyestuffs as they contain sulphonic acid group. The comonomers in polyacrylonitrile range from 0.75-5 %(scheme 12) [82].



$$2\,CH_2{=}\underset{\displaystyle CN}{CH} + CH_2{=}\underset{\displaystyle COOH}{CH} \longrightarrow CH_2\text{-}\underset{\displaystyle CN}{CH}\text{----}CH_2\text{-}\underset{\displaystyle COOH}{CH}\text{-}CH_2\text{-}$$

Scheme 12

The availability of dye sites further improved by copolymerizing with 5–8 % or more of a neutral third monomer such as methacrylate, Vinyl acetate or another vinyl monomer. Terpolymers have better dyeability than the corresponding acrylonitrile copolymers; the neutral monomer is believed to regulate diffusion of the dye into the fibre [83]**.**

Polyacrylonitrile fibres have high melting point and poor solubility owing to the formation of hydrogen bonding between polymer chains [72] **Fig (.1.25)**.

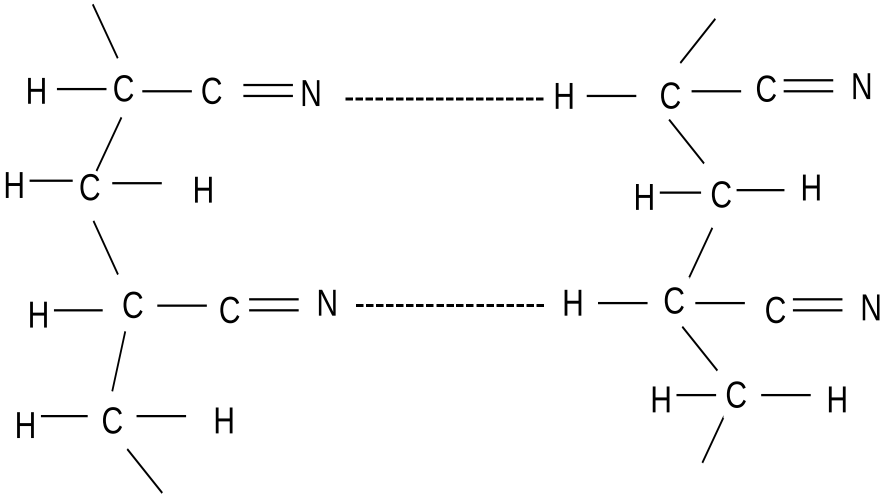


Fig.(1.25): Hydrogen bonding between polymer chains

Acrylic polymer is essentially non-polar. Van der Waal's forces hold the acrylic polymer system together. This seems to be born out by the fact that the acrylic polymer is one of the longest synthetic polymers. That long, non-polar polymer can give useful polymer appears to be confirmed [83].

7.4. Properties of Acrylic Fibres

Acrylic fibres are resistant to attack by most common chemicals (with the exception of a few solvents, such as hot DMF) and are considered inert. They are hydrophobic, resist degradation by light, soften above their glass transition temperature and can be dyed to an extraordinarily wide range of shades of very good fastness properties with the historically maligned basic dyes. The good light fastness can be attributed to the hydrophobicity of the fibres, for it has been shown that the absence of water molecules materially reduces the rate of light fading. Acrylic can also be dyed with disperse dyes but only in light to medium shades of moderate fastness. Due to their desirable features, acrylics and modacrylics find a wide variety of end uses in apparel and home furnishings. One such feature is acrylic's warm soft hand, which has been compared to that of wool although there is no real substitute for wool. Acrylics are intrinsically resistant to light; insect larvae and microbiological attack, and modacrylics have flame retardant properties which make them suitable for children's sleepwear, upholstery and drapes.

7.4.1. Physical Properties

7.4.1.1. Shape and Appearance[84]

Acrylic fibres are available in bright, semi dull or dull luster .

7.4.1.2. Density [72, 85]

The density of most fibres is about 1170 kg/m^3 and increases with the incorporation of halogens.

7.4.1.3. Tensile [87]

The tensile properties of acrylic fibre are little affected by water at normal temperature .

7.4.1.4. Tenacity [72]

It varies from 0.19-0.32 N/tex and elongation to break from 33 to 64 %.

7.4.1.5. Specific Gravity [86]

It ranges from 1.14 to 1.19. Acrylic fibres are often made into high-bulk but light weight fabrics.

7.4.1.6. Moisture Absorption [87]

It is low and about 1 - 2.2 % which may result in rapid drying, contributes to difficulty in dyeing.

7.4.2. Thermal Properties [72, 88]

Acrylic fibres have adequate resistance to heat .It is thermoplastic and responds to heat setting procedures. The fibres degraded or decomposed before melting. Acrylic fibres can be tumble-dried if the drying temperature does not exceed 150 ^{o}C.

7.4.3. Mechanical Properties [84, 89].

Strength of acrylic is fair to good, ranging from 2.0 to 3.5g/d, depending on the type. There is a slight decrease in strength when wet Dimensional stability in acrylic fabric is good with proper heat setting.

7.4.4. Chemical Properties

Acrylic fibres are resistant to most ordinary chemicals.

7.4.4.1. Effect of Alkalis

Acrylic fibres have good resistance to weak alkalis .Concentrated alkalis generally cause rapid degradation [90] .However, surface saponification occurs. This means that any nitrile groups and/or anionic or basic group on the surface of the fibres will react with sodium or cation of the alkali. The fibre surface saponification is gradual. It eventually leads to surface discoloration, yellowing and /or dulling of acrylic textile material [91].

7.4.4.2. Effect of Acids [72, 90]

Acrylic fibres attain good resistance to weak acid and most mineral or organic acids.

7.4.4.3. Effect of Organic Solvents [89]

Solvents used in cleaning and stain removal having no effect on acrylic fibres due to the resistance of acrylic fibres to organic solvents which actually delayed their commercial production, so it was difficult to find a practical solvent for manufactured purposes.

7.4.4.4. Effect of Oxidizing Agent and Detergents [89]

Acrylic fibres are not harmed by house-hold bleaches or detergents.

7.4.4.5. Effect of Sunlight [66]

Acrylic fibres are the most sunlight and weather resistant fibres in common use. The resistance to the atmosphere, which is slightly acidic, is attributed in part to the acid resistance of acrylic polymer.