

CONSERVATION OF ENERGY AND WATER, ECONOMY AND EFFLUENT CONTROL IN PRE-TREATMENT PROCESSES

13.1 Water Consumption in Textile Industry

Textile industry is a leading consumer of water and it ranks among ten top water consuming industries [1]. Table 13.1 shows the approximate consumption of wa-

TABLE 13.1

Water Consumption by Textile Industry in Various Processes [2]

Substrate	Water consumption kg/kg of fabric
Cotton	250-350
Wool	200-300
Nylon	125-150
Rayon	125-150
Polyester	100-200
Acrylic	100-200

ter for the processing of various textile fibres. Cotton fibres require the largest amount of water for its preparation. In general, the water consumption in a process house is about three times the consumption of all other units put together (Table 13.2). The water consumption in the bleaching section is highest. The conventional

TABLE 13.2

Water Consumption Pattern in Textile Mills [3]

Process	Water consumption (% of total)
Bleaching, Finishing	38
Dyeing	16
Printing	8
Boiler House	14
Humidification (spinning)	6
Humidification (weaving)	9
Sanitary, Domestic etc.	9

preparatory processes of textiles namely, desizing, scouring, bleaching, and washing are highly water consuming operations and consequently energy-intensive (Table 13.3).

TABLE 13.3

Consumption of Water and Energy in Kiers and J-Box Processes [4]

Process		Consumption of water l/kg	Consumption of steam kg/kg
	Desizing	3	0.25
	Washing	20	0.35
J-Box	Scouring	2	1.75
Bleaching	Washing	20	0.30
	Bleaching	2	1.00
	Washing	40	0.60
Total		87	4.20
Conventional kier-boiling		100	5.10

13.2 Impurities in Water

The quality of water to be used in a process house decides the ultimate quality of cloth like whiteness, brightness of colour etc. The main impurities in water are turbidity and colour, iron and manganese, alkalinity and hardness. The quality of water received in the textile mills depends on their history. Moorland water is acidic in nature. Colour and turbidity in water may stain the fibre. Impurities in water may deactivate enzymes during desizing and insolubilise starch material which may deposit on the fabric. The Ca^{2+} and Mg^{2+} ions from $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, CaCO_3 and MgCO_3 present in water may combine with soap during scouring. The alkali salt have no or very little aqueous solubility and once deposited the handle, sewability, knittability and water absorbancy of the scoured fabric and yarn will be impaired. Besides dirt will be more difficult to remove from the textiles in hard than in soft water. Ions of heavy metals (iron, copper, manganese) act as catalyst in the decomposition of bleaching agents and cause activated attack with subsequent degradation of fibre. If the iron content of the water supply for reservoir or deep wells is high, oxidation and filtration units must be installed to reduce its content below 0.1 p.p.m., otherwise suitable bleaching auxiliaries must be added to the bleach bath.

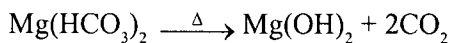
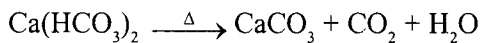
In the aeration technique, the water is pumped through the aeration apparatus [5], the metal is oxidised to its insoluble form and precipitates from the water. Improper water may insolubilise metal oxide during mercerizing and reduce absorbancy and lustre. In the dyeing stage, metal ions may combine with some dyes and cause dulling of shade. Impurities in water may also lead to precipitate on to boiler tubes forming scales. As boiler scale forms, heat transfer and boiler efficiency is reduced forming hot spots which in turn cause weakening of the boiler tubes leading to pipe blow-outs and failures.

The quality of water is judged by total dissolved solids (TDS) and hardness which generally varies depending on the locations and regions. Table 13.4 shows

TABLE 13.4
Acceptable Water Content for Processing [6]

Impurities	Parts per million
Silica	0.5-3
Total hardness (CaCO ₃)	0-25
Total alkalinity (CaCO ₃)	35-64
Dissolved solids (TDS)	65-150
Iron (Fe), Cu, Mn	0.02-0.1
Colour	Transperant
Turbidity	Clear
pH	7-7.5

the approximate idea of the limit of water quality suitable for wet processing of textiles. Water hardness is caused mainly by calcium and magnesium bicarbonates, chlorides and sulphates which can have been absorbed by rain water as it percolates through the various strata. When hard water is boiled, the bicarbonates are decomposed and precipitates as carbonates and the hardness due to these salts largely



disappears. This type of hardness is called ‘‘Temporary hardness’’ and is the major cause of scale formation in boilers. ‘‘Permanent hardness’’ is associated with metal salts such as nitrates, chlorides, sulphates and phosphates which are soluble in water

and are not decomposed by heat. The sum of the temporary and permanent hardness is called “total hardness”. Hardness is usually expressed in degrees and is described in terms of equivalents of calcium carbonate or oxide. It is generally considered that the maximum permissible level of TDS and hardness to be used in wet processing should be about 25 and 500 p.p.m. respectively. Water containing 0-5° English hardness is considered to be soft and over 15° is hard.

1° English hardness = 10 mg/l of CaCO_3 in 0.71

1° American hardness = 1 mg/l of CaCO_3

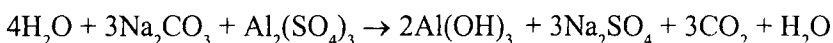
1° German hardness = 10 mg/l of CaO or 7.9 mg/l MgO

13.3 Water Purification

Conventional softening treatment plant may not remove the impurities in water to the recommended permissible level. Demineralised or reverse osmosis technique is needed for removal of TDS from water but is costly. Water purification in the process house normally consists of flocculation, sedimentation, filtration and ion-exchange. Hard water is normally softened using one or combination of methods the details of each process is given in many text books.

13.3.1 Soda-alum process

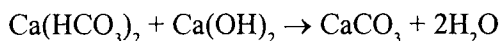
Hard water is first pumped into the reaction tank and then aluminium sulphate is added to it as flocculant. About 20-30 min is allowed to react and then the impurities are allowed to settle for about 30 min before filtration. Many flocculants need alkali



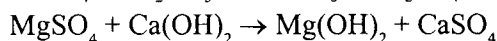
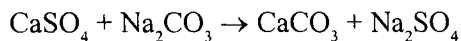
as an assistant flocculant. If additional alkali is not added, the total alkalinity is reduced and part of aluminium sulphate, being water soluble may pass through the filter. As aluminium hydroxide and metals precipitate downwards, clear water arrives at the top and is decanted.

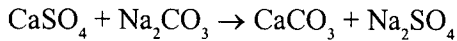
13.3.2 Lime-soda process

In this process lime and sodium carbonate are added to precipitate the calcium and magnesium salts as temporary hardness.



For permanent hardness the reactions are :

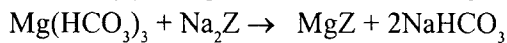
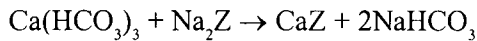




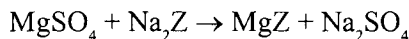
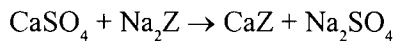
The softened water is usually slightly alkaline with 1-4° residual hardness.

13.3.3 Base exchange process

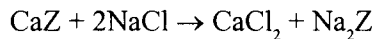
When hard water is passed through a bed consisting of zeolites, which are synthetic material systems composed of complex sodium, aluminium and silicate salts (Na_2Z), the calcium and magnesium ions are exchanged. The displacing reactions for temporary hardness are :



For permanent hardness the reactions are :



The process is reversible and the bed (Na_2Z) can be regenerated by passing concentrated salt solution. This method of water softening yields a very soft water (0.5-1° hardness).



Water softening by demineralisation systems can be accomplished using either mixed bed (both cation and anion resin in one bed) or two bed system (resins remain separated according to their charges). The active sites of the resins are limited and the sites are filled when water passes through these columns and must be regenerated again. Their ion-exchange capacity is greater than that of zeolite.

13.4 Economy Through Energy Conservation

The textile industry consumes both electrical and thermal energy. All the four major commercial energy sources i.e. coal, electricity, oil and gas are utilised. Power from hydroelectric, nuclear power and natural gas also contributes important source of energy, solar energy, bio-gas may be used for textile drying, for heating water, singeing, desizing, kier-boiling etc. [7-11]. About 55 to 60% energy consumed in the textile industry is used in various pre-treatment stages. Table 13.5 shows the pattern of steam consumption in a composite textile mill. Wet processing of textiles consume only a small proportion of electrical energy ($\approx 15\%$) mainly for running various processing machineries. Fuel in terms of coal or oil is used extensively in the textile industry and thermal energy in the form of steam generated in the boiler is supplied to the various equipment through pipes. Several plants/machin-

TABLE 13.5
Steam Consumption in a Composite Textile Mill

Department	Steam consumed (%)
Humidification	10
Sizing	15
Boiler house (auxiliaries, blow down etc.)	05
Leakage and avoidable wastages	10
Wet processing	60

ery developments and technological advancements have been witnessed over the last decade to meet the challenges for conserving both thermal and electrical energy. Some of the important approaches are given below.

13.4.1 Efficient generation of energy and minimum consumption

The boiler itself should be very efficient to generate steam and for this preparation of oil, air to fuel ratio, stack temperature of flue gases, conversion of furnace oil to LSHS oil, maximum condensate recovery, cleaning of the fire side, replacement of old boilers etc. are the various important factors to be taken care-of. Factors responsible for optimum consumption of steam such as supply of steam at correct pressure, provision of pressure reducing valves, water separators in steam lines for supply of dry steams at requisite pressure, selection of trap of right type and size for efficient recovery of condensate etc. should be considered for the saving of thermal energy.

13.4.2 Mechanical removal of water before drying

Use of squeezing systems to pick-up 40-50% water by using Kuster mangle [12], Rotomat washing machine [13], Kleinewefers Jaeggli Bioflex [14], Aquilan air cushion squeezing [15] and Roberto rolls in place of rubber rolls [16] are some of the machineries related to efficient removal of water/process liquids or controlled application. Use of vacuum impregnation technique [17, 18] and vacuum roller extractor [19] claim 75% fuel saving by the use of vacuum for expulsion and expansion of air from the fabric for better and uniform impregnation. Use of suction slot for mechanical removal of water for fuel saving is also reported [20].

13.4.3 Increased efficiency of drying and heat-setting

The total energy consumed in wet processing may be in heating water, 35-65%;

drying, heat-setting or baking, 25-60% ; liquor circulation, 10% ; the rest is consumed in moving and handling fabric and so on. Increased efficiency of drying is achieved by improved thermal insulation, reduced leakages, appropriate steam pressure and proper steam line distribution. Use of radio-frequency technique in drying can be used as low energy electromagnetic radiation. High speed heat-setting system can be developed by the use of mixture of air and superheated steam and swelling compounds like polyethylene glycollic ether in place of conventional hot air can be used and 60-70% saving in thermal and electrical energy is thus, possible.

13.4.4 Reduced liquor to material ratio

Generally, machines with bigger trough sizes cause major wastage of water and chemicals. V-shaped troughs give better impregnation time with low liquor ratio and the quantity of steam required for heating the liquor is also less. Further, switching over to semi-continuous or continuous operations can also lead to reduced liquor ratio, time and cost. The spraying of liquor, nip padding, foam application, minimum application techniques etc. are also the various approaches in this direction.

13.4.5 Efficient heat recovery

In the process house water is generally heated from room temperature to 80-90°C and at the end of the process water is run away into the drain. This is absolutely uneconomic. Many of the modern machine is equipped with effective heat-exchangers, in which the outflowing hot water heats up the inflowing cold water and is only then discharged into the drain.

Another possible source of recoverable heat is the waste heat contained in the condensate. Owing to the condensation problems, the flue gas temperature is around 200°C. If the flue gases are cooled down from 200°C to 50°C by boiler feed water or processing water, the result is considerable saving in energy.

Exhaust air heat recovery units can also be employed as the energy carrier may be gas or air. During heat-setting of textiles on stenter frames emission of compound capable of vaporisation may occur and the flue gases is escaped from the chimney. The air exhausted from the stenter is fed through an insulated air duct into the boiler house, where together with the quantity of air required for combustion, is passed through a blower system into the the boiler. When the boiler comes into operation, clean flushing energy is drawn-in through an intake via a switch equipped with an automatic drop flap. The switch changes over to exhaust air after the burn-

ing unit has ignited. Above the roof is an open buffer chimney, through which the excess exhaust air can escape or the fresh air required for further combustion can be drawn-in [21].

13.4.6 Heat recovery from process effluents

Textile processing houses discharge a lot of contaminated hot waste water and emit smoke, which are sources of water and air pollution. There is an inter-relationship of energy recovery and environmental protection. Increased temperature have negative effect on the organisms living in water and destroy the ecological system. The waste water and exhaust gas can be used to heat up clean, cold water and this can be returned to the production process.

13.5 Economy Through Water Conservation

It is always essential to use less quantity of water with proper quality for a particular process. The cost of water is increasing and in order to conserve energy it is necessary to reduce the water consumption in the process house. This is expected to result in savings of chemicals, water, reduce the effluent quantity and related problems of treatment and disposal. Machineries with new designs and new process techniques are developed for minimising the requirement of water.

13.5.1 Minimising liquor to material ratio

Reduced liquor ratio not only reduces water consumption but also reduce the quantity of effluent to be treated. The liquor ratio in kier and peroxide boil, usually ranges from 2.5 to 4. In pressure boils, the water consumption for cooling and washing is found to vary from 6 to 9 litres/kg of cloth. It is possible to reduce the water consumption by about 25% by regulating the water particularly at the time of cooling and washing operations with the help of water meter or timer. The aspect of liquoro ratio is already discussed while describing the conservation of energy through plant and machinery modification.

13.5.2 Minimising wash liquor

Washing machines are the major consumer of water. Generally old type of washing machines like slack and tight rope require more quantity of water for washing. Counter-current principles of washing, aquatex washing, beam and suction washing, powerful jet with pumps and vibrators, horizontal or inclind washers etc. will not only increase the washing performance but also decrease the water consumption.

13.5.3 Re-using rinsing bath water

Water and heat energy consumption, together with effluent accumulation can be reduced in batch type bleaching of textiles by re-using rinsing and treatment baths on the counterflow principle [22]. This system has been patented under the name Bleachstar. Due to the better usage of the individual baths, large quantities of clean water and heat energy are saved.

13.5.4 Direct steam injection

For reducing fresh water requirement in a boiler, direct steam injection in jiggers and other equipment may be replaced with indirect heating system. The continuous machines offer, besides reduction in quantity of water with better washings and labour requirement, produce more even quality of fabric. By proper cleaning and sequencing one can avoid down time during continuous processing operations.

13.6 Economy Through Process Modification

Process modifications/developments for minimising energy consumption in the pre-treatment processes are very important and some of the major developments are briefly mentioned.

13.6.1 Mather and Platt's Vaporloc bleaching

Vaporloc system is a continuous washing and bleaching unit with a reaction chamber for scouring under steam pressure of about 30-40 p.s.i. at 130-140°C for 60-80 sec, followed by washing and peroxide bleaching in another chamber. Considerable savings in steam, time, labour are achieved. Only 3-7 min is required for scouring and bleaching. Reducing the time of treatment by modifying the pressure kler boiling for 2-6 h at 15-25 lb/in² in presence of sodium sulphite in the scouring bath is recommended [23].

13.6.2 J-Box bleaching

Du Pont Co. has developed a two minutes bleaching process [24] for heavy fabrics using H₂O₂ at very high pH values using a special formulation to prevent undue decomposition of peroxide and damage of fabric during the process.

13.6.3 Solvent Scouring

“Markal Process” developed by ICI for desizing and scouring of fabric involves the treatment of a suspension of enzyme, TCE and surfactant solution [25]. The material after treatment for 10-20 sec passes through a steaming chamber where the solvent is flashed-off. About 80% saving in steam consumption is reported.

13.6.4 Cold bleaching

A cold bleaching method is reported in which decomposition of NaClO_2 is caused by acidification or by addition of reducing agent [26]. Sodium hypochlorite is an intermediate in the release of active chlorine dioxide. A combination of bisulphite with an aldehyde is said to initiate the cold bleaching action and practically no thermal energy is required. The use of azetropic/emulsion based scouring cum bleaching formulation helps in processing at room temperature. This process uses a hot wash at not less than 70°C to achieve the required result. In the cold pad-batch method, the use of peroxide, sulphates and some accelerators like urea, glucose, penta-acetate etc. can cause considerable savings in energy, water and labour.

13.6.5 Combined processes

Several single stage combined pre-treatment processes are discussed in Chapter 11 to minimise the energy consumption. In recent years there has been a trend to save labour and energy by combining different processes with dyeing operations. The combined mercerizing and scouring process consists of impregnating the fabric with caustic soda of mercerizing strength at elevated temperature with a steaming unit within the hot mercerizing section [27]. In the Bruckners Remaflame Process [28] for combined drying and finishing, a mixture of methanol and water is applied to the fabric along with finishing solutions. As the fabric is moved rapidly upward through the drying chamber, methanol is ignited, the solution burns away and the fabric is left with less than 4% moisture. Remaflame dryers have been claimed to give fuel efficiency as high as 72% as compared to 50% for conventional dryers.

13.6.6 Shortening of process sequence

The time of various pre-treatment processes can be reduced by judicious approach of the shortening of process sequence without compromising the quality of goods. The heat-setting speed can be improved by making use of super-heated steam and some swelling compounds instead of hot air. Grey mercerization can reduce the number of drying operations. Running two or more ends side by side or superimposed on machines like shearing, cropping, chainless mercerizer, cylinder drying range etc. can increase the production. Hydrosetting of synthetic fibres and its blends at HT/HP beam dyeing machine can reduce the energy consumption. Combined optical brightening and heat-setting for synthetic fibre fabrics and combined bleaching and optical whitening are commonly employed.

13.7 Pollution Aspects in Pre-treatment Processes of Textiles

13.7.1 Water and air pollution

The two main sources of pollution in chemical pre-treatment of textiles are water pollution and air pollution. Water pollution is mainly attributable to the various waste stream coming out of the pre-treatment operations like desizing, scouring, bleaching etc. Moreover, the blow down water from the boilers and the effluent discharged from the water treatment plants also contribute to the water pollution. Air pollution mainly comes from the boilers which are used to produce heat energy requirements for wet processing. The extensive use of coal, oil, gas for industries has led to the air pollution. Polluted air contains cotton dust, CO, nitrous oxide (NO_x), sulphur oxides (SO_x), CO_2 , CH_4 , chemical vapour, various oxidation colours, chlorine vapour, kerosine, various hydrocarbons and particulates in the atmosphere. The worst condition for human health is the combination of particulates containing SO_2 . Generally, air pollution from industrial fuel burning and processing emission contribute to about 30% of total air pollution. In case of industries situated near housing colonies, the permissible limit of any harmful material in air is mentioned as $1/100$ of the MAK value. If the values are higher than this permitted level, an air purification system will have to be installed. Usually the emissions are ducted away by means of a tall chimney to minimise the impact of air pollutants. Green house gases like CO_2 , CH_4 and N_2O etc. trap the earths heat, raising atmospheric temperature. The impact would be varied and unpredictable. A key effect may be rising of sea level by around 50 cms by 2100 because of expansion due to heat and melting of glaciers. This may become a cause of submersion of low lying areas and displacement of around 80 million people. The main culprit causing global warming is CO_2 , whose contribution is about 87% and hence CO_2 emission is required to be contained. Table 13.6 summerises the possible problems in environmental control likely to be caused by individual steps in the production of textiles. Air pollution due to scouring and bleaching operations are considered to be negligible as not many volatile products are used at high temperatures. Actic acid is volatile and readily eavporated in the chamber. It can be replaced by citric acid which is non-volatile and also will be required in a lesser quantity.

To minimise waste water pollution some of the most frequently used chemicals have already been either banned by law or voluntarily withdrawn. The red listed

TABLE 13.6

Environmental Problems at Various Stages of Chemical Processing of Textiles [29]

Processing step	Waste water pollution	Air pollution
<i>Spinning/Texturising</i> (yarn production) dry step	No	Heat energy given out
Weaving (winding/dry) (warping/dry) (sizing/wet) Drying	Leads to pollution later on desizing	Heat energy
<i>Chemical processing</i>		
Singeing	No	Heat energy
Desizing	50% total load	No
Scouring/bleaching	20% total load	No
Dyeing	Dyes, Chemicals	Some
Printing	Dyes, Chemicals, Thickeners	Some
Finishing (Conventional/ special)	Natural and synthetic polymers, chemicals	Appreciable

chemicals, whose presence on a textile product considered as dangerous can be divided into following groups :

- (i) Pentachlorophenol – used as preservatives for gums, sizing agents, fungicides, rot proofing agents. Its range limit is 0.05 p.p.m. to 0.5 p.p.m.
- (ii) Heavy metals – present in buttons, dyes, antiseptics, fungicides, auxiliaries, after-treating agents. Its range limit is 0.0001 to 100 mg/kg.
- (iii) Toxic pesticides – to prevent pest attack in cultivation of wool and cotton, 0.5 to 5 mg/kg.
- (iv) Formaldehyde – resin finishing, dye after-treatments, printing assistants etc., 20-300 p.p.m.
- (v) Azo dyes – those which could release listed carcinogenic amines, during reductive cleavage (Banned).
- (vi) Halogen carriers – used in the dyeing of disperse dyes on polyester, 200 mg/kg for volatile organic helogens.
- (vii) Chlorine bleaching – to be avoided under some eco levels.

13.7.2 Parameters for assessment of harmful materials in waste water

It is an established fact that industries produce significant quantities of contaminant waste water which are discharged to municipal gutters, open lands, rivers, nullah and ponds and ocean and cause considerable pollution problems. Pollution in some parts of the world has reached a level close to ecological catastrophe and all countries are tightening control on environmental pollution. It is now essential that the waste water be treated before being discharged to the sewerage system and has to be biologically degradable. These harmful substances are assessed together as some parameters (Table 13.7) which can be evaluated by standard test methods.

TABLE 13.7

Parameters for Assessment of Harmful Materials in Waste Water [30]

Parameter	Estimation method	Concentration (unit)
BOD	Oxidation by aerobic micro-organism	mg O ₂ / l
COD	Oxidation with K ₂ Cr ₂ O ₇	mg O ₂ / l
TOC	Catalytic burning	mg C / l
DOC	Catalytic burning	mg C / l
AOX	Adsorption on active carbon	µgx / l
N total	Colorimetric estimation	mg N / l
P total	Precipitation	mg p / l

Physical, chemical, physico-chemical and biological treatments are used to test the nature of textile effluents. The physical characteristics include temperature, pH, colour etc., whereas chemical characteristics include the nature and quantity of organic and inorganic compounds and dissolved gases. The biological characteristics include different types of micro-organisms or microbes that are present in the effluent. These characteristics are determined in terms of BOD (biological oxygen demand), COD (chemical oxygen demand), THOD (theoretical oxygen demand) and TOC (total organic carbon) etc.

The tolerance limits (Indian Standard Institute) for industrial effluents, textile industry raw waste water characteristics are given in Table 13.8. The tolerance limits are different for different receiving bodies. Such regulations are imposed to facilitate further purification of water by sewerage authorities, which can then be discharged into river or other major water sources. Table 13.9 lists some typical

TABLE 13.8
Tolerance Limit for Industrial Effluents [31]

Characteristic	Tolerance limit, mg/l			
	A	B	C	D
Suspended solids	100	600	200	100
Dissolved solids (inorganic)	2100	2100	2100	–
pH Value	5.5-9.0	5.5-9.0	3.5-9.0	5.5-9.0
Temperature, °C	40	45		45
Oils & Greases	10	20	10	20
Total residual chlorine	1	–	–	1
Ammoniacal nitrogen (as N)	50	50	–	50
Total Kjeldahl nitrogen (N)	100	–	–	100
Free ammonia (as NH ₃)	5	–	–	5
Biochemical oxygen demand (5 days at 20°C)	30	350	350	100
Chemical oxygen demand	250	–	–	250
Lead (as Pb)	0.1	1	–	1
Cadmium (as Cd)	2	1	–	2
Hexavalent chromium (as Cr ⁺⁶)	0.1	2	–	1
Total chromium (as Cr)	2	2	–	2
Zinc (as Zn)	5	15	–	15
Percent sodium, max.	–	60	60	–
Residual sodium carbonate	–	–	5	–

A – Effluents discharged into inland surface waters

B – Effluents discharged into public sewers

C – Effluents discharged on land used for irrigation

D – Effluents discharged into marine coastal areas

ratios of general effluents. Generally, the treatability of the effluent is illustrated by ratio of COD to BOD. COD quantifies the total oxidisable portion of the effluent. BOD is a measure of the biologically oxidisable portion of the effluent. The higher the ratio of COD/BOD, the less treatable the effluent. The organic carbon is oxidised to CO₂ which is expressed as TOC [33]. A strength and treatability similar to domestic sewage is the objective.

TABLE 13.9
Typical Ratios of General Effluents [32]

Operation	Typical COD/BOD ratio
Domestic sewage	2.1
Brewing	1.6
Textiles	1.6-6.0 (average 3.0)
Chemical manufacture	3.6
Abattoir	1.9

13.8 Pollution Loads in Pre-treatment Processes

The nature of textile effluents is very complex as various types of fibres and chemicals are employed in preparing the textiles. Further the process sequence and chemicals employed in the pre-treatment processes vary from fibre to fibre. The quantities of pollutants that form the pollution load going into the waste water thus depend on the amount and kinds of fibres, type of manufacturing operation employed and water consumption practices.

Approximately 45 million tons of fibres, of which over 50% are cotton, are consumed each year for textile purposes [33]. Although synthetic fibres do not contain any natural impurities, they produce considerable amount of pollutants during wet processing. Table 13.10 gives the characteristics of different processes wastes

TABLE 13.10
Pollution Loads of Cotton and Wool in Pre-treatment Processes [34]

Process	Water required (l / kg)	BOD (mg O ₂ / l)	COD (mg O ₂ / l)	Pollution load (%)
<i>Cotton</i>				
Desizing	15-20	3000-6000	4000-6000	>50
Scouring	4	8000-14000	7000-12000	10-25
Bleaching	150-180	800-1200	80-150	3
Mercerizing	7	7-50	10-70	<4
<i>Wool</i>				
Scouring (raw wool)	10-40	22000	42600	—
Milling	5-18	4000-24000	6000-4300	75
Carbonising	30-80	200-500	200-700	1

from different stages in pre-treatment of cotton and wool fibre/fabrics. In case of cotton sizes are the major factor being responsible for almost 75% of the pollution load. In case of wool, however, the natural impurities in the unwashed fibre amount for 30-50% of the pollution load. The agents used in synthetic fibres which also cause water pollution are listed in Table 13.11. The materials which can cause sig-

TABLE 13.11

Characteristic Effluents from Processing of Synthetic Fibres [35]

Fibre	Water consumption l / kg of fibre	pH	B.O.D. p.p.m.	Pollutant	% o.w.f
Viscose Rayon	45	7-9.5	1200-1800	Sulphonated oil,	2.0
				Antistatics,	2.0
				Detergents,	3.0
				NaCl.	10-30
Acetate Rayon	85	7-9.5	500-800	Sulphonated oil,	2.5
				Antistatic,	1.5
				Detergents,	1.0
				Softeners.	2.0
Nylon	140-200	7-9.5	300-500	Sulphonated oil,	2-4
				Antistatics,	1.5
				Detergents,	1.0
				Fatty matter.	1.0
Polyacrylics	140-200	1.5-3	500-700	Formic acid,	3.6
				Copper sulphate,	3.0
				Antistatics,	1.5
				Detergents,	5.0
Polyesters	140-200	1.5-3	300-800	Carriers.	2-10
				Antistatics,	1.5
				Detergents,	3.6
				Acetic acid,	4.0
				Carriers.	6-40

nificant water pollution in synthetic fibre wet processing are spin finishes, coning oils, anti-static agents, synthetic detergents, sizes, thickeners etc. The waste water

of synthetic fibres are highly variable and a general characterisation of these wastes is useful only as an approximate indication of their consumption [36].

13.8.1 Desizing effluents

Sizing agents and lubricants are needed for producing textile materials. Sizes used for weaving can be generally classified into four main classes i.e. starch, PVA, CMC, acrylates and others. During the desizing process they get into the effluent. The effluent is further loaded by the chemicals (enzymatic or oxidative) used in desizing apart from the sizes and lubricants [37]. Additional effluent loads during desizing are also produced by fungicides which are mixed in with the sizing agents to preserve them. Size has also a tendency to cause mildew, algae etc., to form in ponds and in slow moving streams. Thus, the discharged effluents account for approximately 50% of the COD level in pre-treatment processes. The proportion of water consumed in this process is comparatively small. Significant characteristics of the effluents of this process are high BOD, high TDS and some suspended solids, which are sometimes in colloidal form. However, the nature of sizing agent used decides the BOD of the wash liquor (Table 13.12). Native and depolymerised

TABLE 13.12
Oxygen Demand of Various Types of Sizes

Type of size	BODs mg O ₂ / kg	Oxygen consumption kg O ₂ per 1000 kg of textile material
Corn starch	810,000	477
British gum	690,000	690
Methyl cellulose	1,600	1.6
C.M.C.	10,000	9.0
Poly (vinyl) alcohol	1,600	1.6

starches as well as esterified are easily biodegradable. But other products such as CMC or PVA are not satisfactorily degraded and are present a more or less persistent form of pollutant in the upper layers of waste water (Fig. 13-1) [38, 39]. A possible solution to reduce the oxygen demand of starch sizes is the use of persulphate to replace enzyme degradation. Unmodified polyacrylates are also difficult to be degraded biologically and remain as polyelectrolytes in the aqueous phase. By intro-

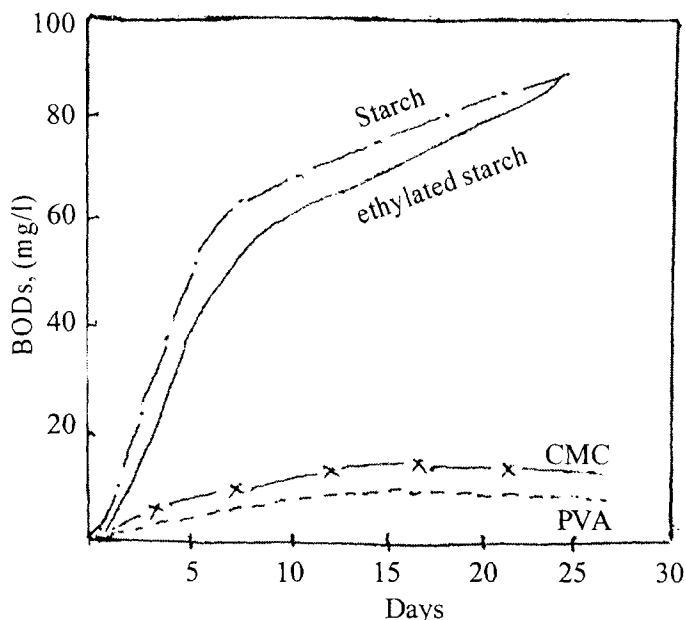


Figure 13-1. Oxygen demand of various types of sizes [40].

ducing the hydrophobic groups, a satisfactory elimination from the aqueous phase is possible biologically. Another approach to minimise the pollution problems is to use a mixture of modified natural polymers with good biodegradability and synthetic polymer with ease of recovery and re-use. Cationic modified product and guar gums are easily degraded by microorganisms and their mixtures with suitable starch derivatives (1 : 4).

13.8.2 Scouring effluents

The chemicals used in the scouring process are mainly, alkalies, wetting agents, detergents, sequestering agents etc. About 25-40% of total water used in a composite mill is consumed in this section. In the scouring process impurities are removed from the fabric depending on the kind of fibre. Generally, oil, colouring matter, detergent, antistatic, lubricants, solvents, oligomer etc. in the presence of alkali contribute to water pollution. Significant characteristics of effluents discharged from scouring section are high BOD, high temperature (70-80°C), very high pH (10-12) and high TDS.

Non-biodegradable branched chain anionic surfactants are now replaced by readily biodegradable straight chain compounds and thus pollution load in waste

water is reduced [41]. Non-ionic ethoxylated alkyl phenols which are extremely used for scouring are difficult to biodegrade at low temperature. Excessive foam of the surfactants may seriously affect the efficiency of biological waste water treatment.

Conning oils, solvents and antistatic agents removed from the fabric during scouring are generally inert to biological treatments [42, 43]. Coagulation with calcium chloride is useful for removing conning oil or alternatively floatation method can be used.

Scouring of wool is mainly done by detergent and solvent. The main components of wool scouring waste water are wool grease, suint and dirt and excrement. Table 13.13 shows the pollutant load of the wool scouring effluent. The detergent

TABLE 13.13
Pollutant Load of Wool Scouring Effluent [44]

Parameter	Concentration unit
COD	60,000-90,000 mg O ₂ / l
BOD	30,000-50,000 mg O ₂ / l
Pesticides as total of individual pesticides	0.4-1 mg / l
AOX, adsorbable halogenated hydrocarbon	ca.1.0 mg / l
Nitrogen, Total of ammonical, nitrate and nitrite N ₂	1000-1500 mg / l
Phosphate	20-30 mg / l

process involves washing of greasy wool with hot water in the presence of non-ionic detergents and sodium carbonate. The characteristics of the discharge are generally affected by both the wool origin and the pre-treatment system which is used to extract the grease and wool waxes. Grease causes big problems as it is not biodegradable. It is possible to reduce the concentration of grease by recovery, but it will still remain high for biological systems.

13.8.3 Bleaching effluents

Generally, the bleaching waste liquor in cotton processing is alkaline in nature with BOD 3.5% of the total load. Hypochlorite is still used as a bleaching agent for cotton due to its bleaching power at low temperatures and its relatively low cost. However, the formation of highly toxic chlorinated organic by-products (AOX) during the bleaching process has limited its use because these types of compounds

are a potential hazard to the drinking water resources when discharged [45, 46]. Table 13.14 shows the typical data on the total AOX and CHCl_3 concentrations in

TABLE 13.14

AOX and CHCl_3 Concentrations in Bleaching Liquid (p.p.m.)

Toxic by-products	NaOCl stage	H_2O_2 stage	Rinse 1	Rinse 2
AOX	105	19	5	2
CHCl_3	11.5	1.1	0.3	0

spent hypochlorite bleaching liquids and rinse solution. Chloroform can be reduced to virtually zero by subsequent peroxide bleaching and hot washing. Generally bleaching with H_2O_2 is less harmful as far as AOX content in the waste water. H_2O_2 decomposes into water and oxygen and leaves little dissolved solids or objectionable residue behind except small amounts of sodium silicate and alkali that is added to peroxide liquor. The commonly used stabilisers like DTPA or phosphonates are not easily biodegradable. A new class of sugar acrylate complex sequestering agents are developed for ecological alternative for the present range of products used [47].

Peracetic acid is environmentally safe since it decomposes to acetic acid and oxygen [48, 49]. However, acetic acid contributes slightly to higher BOD levels of waste water in the order of magnitude of 20-40 mg BOD/l. Bleaching of synthetic fibre does not create a major water pollution problem. In case of sodium chlorite bleaching, the sodium nitrite added to the bleaching bath causes water pollution. The sodium sulphite used as an antichlor is also not desirable in water. A low concentration of optical brightening agent do not create any special pollution problem, although most of the agents are not biodegradable within 5-10 days of waste water biological treatment [50]. In contrast, however, some of the intermediates used for the production of optical brightening agents are more or less toxic.

13.8.4 Auxiliary effluents

The consumption of surfactants in textile wet processing is very high and thus large number of surfactants find their way into waste water. Textile auxiliaries used in pre-treatment have relatively lower pollution loads. The ethylene oxide/propylene oxide condensates of fatty alcohols and alkyl phenol ethoxylates (Fig. 13-2) are most commonly used product groups for wetting/detergency. However, during the last few years, it has been shown that during biological degradation of alkyl

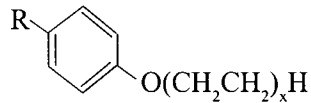


Figure 13-2. Structure of alkyl phenol ethoxylates

phenol ethoxylates, metabolates are produced which are toxic to fishes. By careful selection of alkyl phenol ethylene oxide it is possible to achieve a degree of biodegradability, but the decomposition products are still phenolic and therefore toxic to fish. Fortunately, non-ionics like ethoxylated fatty alcohols (Fig. 13-3), are more



Figure 13-3. Structure of ethoxylated fatty alcohol. Figure 13-4. Structure of polyacrylate.

degradable and whose metabolites are non-toxic. Another eliminable dispersing agent is low molecular weight polyacrylate (Fig. 13-4). The fat emulsifying power of Lauryl Alcohol Ethoxylates is of importance in pre-treatment of fabrics as chlorinated products are discharged. In order to remove fatty stains, the emulsifying power has to be higher than 10% of fat quantity. Lauryl Alcohol Ethoxylates have a higher foaming tendency and the problems are aggravated in the presence of sizing polymers which have a foam stabilising effect. Anionic alkyl benzene sulphonates are hard compounds in the sense that they are resistant to break down by bacteriological action in waste treatment plants. The low rate of biodegradability is due to the presence of branched side chain. If the linear side chain is present, the rate of degradation increases markedly. Cationic surfactants are used in small quantities for specialised purposes. These are neutralised or rendered non-surface active by reaction with anionic substances which are present in most effluents from textile works.

13.9 Waste Water Treatment From Pre-treatment Plants

Selection of the appropriate method of treatment is influenced by a large number of factors related to each effluent characteristic, such as relative costs, levels of treatment required or site restrictions etc. The composition of a textile effluent depends not only on the type of mill but also to a great extent on the processes involved. Various mechanical, physical and chemical methods can be used, depending on the composition of the effluent. These methods are summarised in

Fig. 13-5. By several techniques and treatments, passing through several stages of

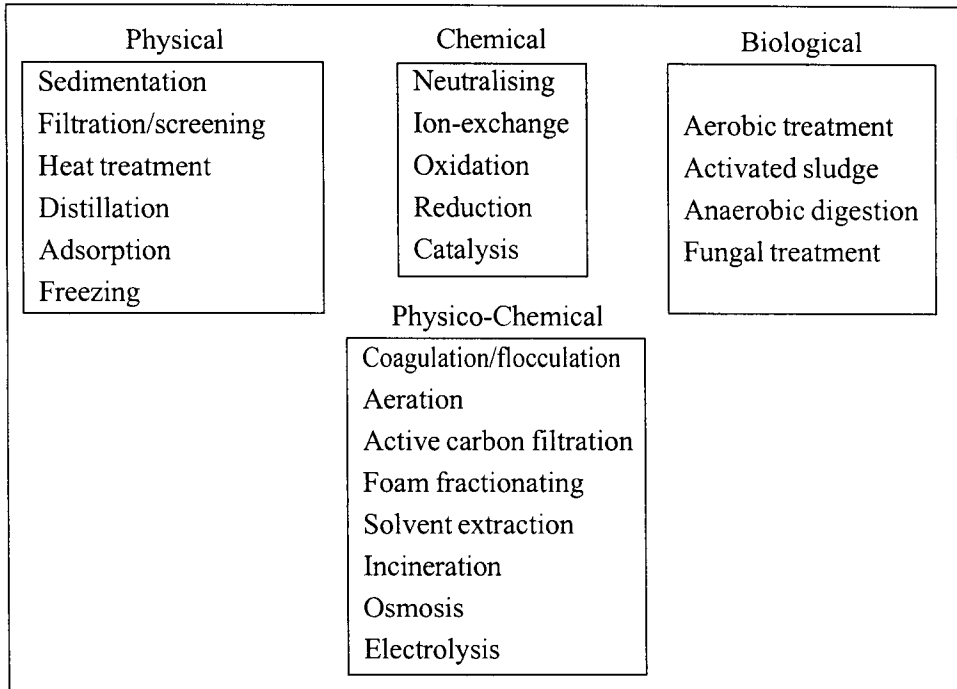


Figure 13-5. Physical, Chemical and biological treatments.

purification, it is possible to obtain water sufficiently clean to be recirculated in a textile mill, as in other spheres of industry. Generally, there are four stages of effluent treatments – namely, preliminary treatments, primary treatments, secondary treatments and tertiary treatments.

Preliminary treatment processes remove grit and solid matters. This include screening, sedimentation, floatation and flocculation. Primary treatment processes are intended to fit effluents for admission to secondary treatments. It includes equalisation, pH adjustment, neutralisation and possible disinfection. These preliminary and primary treatments of the effluent are necessary whether the discharge is to the municipal treatment works or direct to a water course (Fig. 13-6). The variations in loading are eliminated by mixing highly concentrated waste with very dilute waste i.e. equalisation. Neutralisation is done by adding H_2SO_4 or HCl or using flue gases [52] to pH 7. If neutralisation is done by using HCl, sodium chloride is formed, which cannot be dumped in rivers due to salt burdening of river

Conservation of Energy and Water

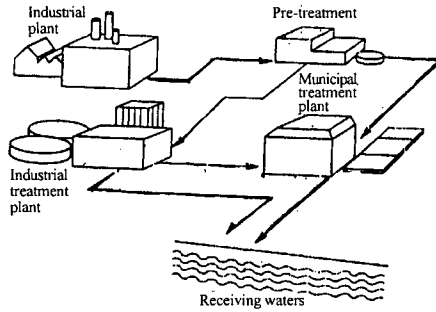


Figure 13-6. Waste water management activities [51].

water. In addition the building structures and production equipment are subjected to corrosion by acid vapour. The H_2SO_4 leads to the formation of sulphate which has adverse effect on concrete. The use of flue gas has several advantages over mineral acids [53]. Flue gas is easily available from boiler firing installation. During neutralisation bicarbonates are formed which are advantageous to the environment. A process for the treatment of effluents using flue gas is shown in Fig. 13-7.

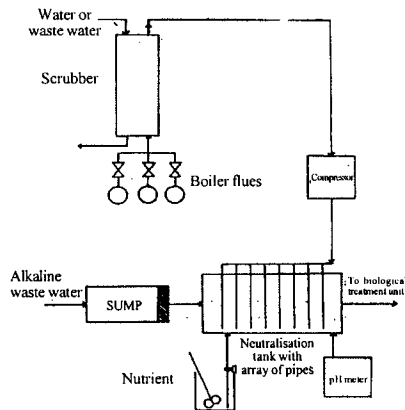


Figure 13-7. Process flow diagram for neutralisation of flue gas.

The secondary treatment methods are used to reduce the organic load of textile effluents. It consists of aeration, chemical coagulation and biodegradation. Aeration helps in reducing the possibility of odour formation and sludge production. Effluent contains impurities in dissolved, colloidal and suspended form. Precipitation and coagulation of these impurities to produce microflocs is done either by pH adjustment (such as acid cracking), or by inorganic coagulants (multivalent metals)

or by organic coagulants. Acrylic acid base size can be completely removed from effluent by precipitation. Commonly used coagulants are lime, ferric sulphate, ferric chloride, ferric alum, calcium chloride, aluminium sulphate, sulphuric acid etc. Organic coagulants are low molecular mass, highly charged polyelectrolytes that are usually cationic, and can be used either as an alternative to, or in conjunction with, inorganic coagulants. Their mechanism can be explained in terms of the charged patch model (Fig. 13-8). When the impurities in the waste water are in the form of

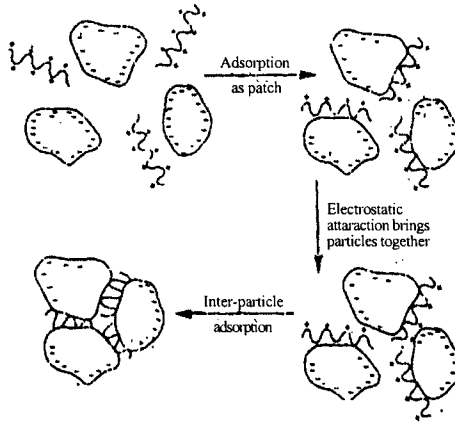


Figure 13-8. The 'charge patch' coagulation model.

microflocs and other suspended solids, the second stage of flocculation aggregates them into larger agglomerates. Flocculation involves adsorption of the polyelectrolyte onto particle surfaces. These form loops and tails which act as physical bridges across the particles, thus binding them together into a polymer-particle matrix or floc i.e. a bridging mechanism (Fig. 13-9). A substantial proportion of colloidal

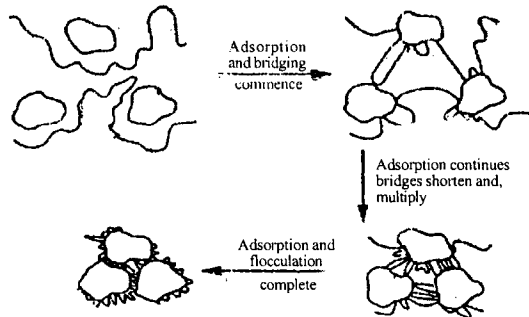


Figure 13-9. The 'bridging' flocculation model.

dirt (stabilised by detergent) from wool scouring effluent can be removed by flocculation process (Fig. 13-10) with high molecular mass bridging flocculant like

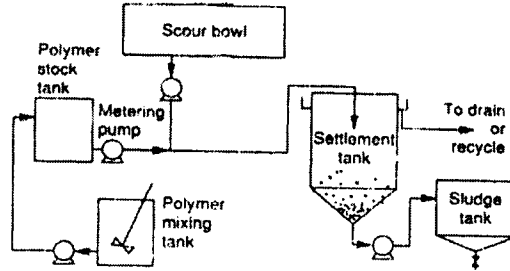


Figure 13-10. Flow diagram of a typical wool-scour treatment plant.

polyelectrolyte with slight anionic or cationic charge depending on the particular characteristics of the liquor to be treated. Recycling of the liquor to the scouring bowls is also possible. Conventional centrifugation, floatation or settling is broadly used for grease and suspended solid removal from wool scouring waste water. Hot acid cracking also increases grease removal. Grease removal before biological treatment will greatly increase the load removal. Typical reductions in suspended solids (and the accompanying reduction in COD) are shown in Table 13.15. Grease re-

TABLE 13.15

Typical Data from Treatment of Wool Scour Effluent

Treatment	COD		SS	
	(mg/l)	Reduction (%)	(mg/l)	Reduction (%)
Untreated	100490		30950	
Centrifugation 60 mg/l Zetag 92	91500	9	26200	15
Centrifugation 100 mg/l Zetag 92	60460	40	19370	37
Centrifugation	50650	50	13400	57

covery by centrifugation is usually less than 50%. Another system of wool scouring waste water treatment is by land irrigation [54]. The treatment steps are, storage and aerobic digestion by static aeration, land farming and evapotranspiration of land farming leachate.

In biodegradation, the micro-organisms are utilised to degrade the organic ma-

terials in the waste stream. Aerobic bacteria requires oxygen while anerobic bacteria thrive in the absence of oxygen. Microbes consumes organic matter giving out finally gaseous products. The most common aerobic biological treatment processes are activated, trickling filters [55]. A schematic flow chart for activated sludge treatment is shown in Fig. 13-11. The activated sludge process involves mixing of

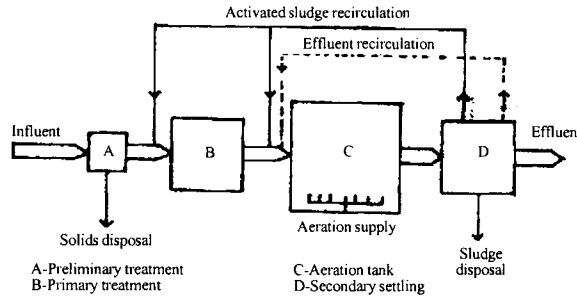


Figure 13-11. Activated sludge plant.

incoming waste water with biologically active sludge or suspensions of microorganisms. The mixture is then aerated with compressed air or mechanical aerators for the desired length of time before transferring the same into another tank where the aerated sludge is separated by sedimentation. The treated effluent is then discharged to the natural streams. Biological systems as activated sludge and aerobic filters have been widely used to achieve strict standards in wool scouring waste water treatments. The removal of sizing agent by aerobic biodegradation is restricted almost entirely to natural products like starch. The starch is usually decomposed by bacteria with the aid of specific enzymes into its fundamental building blocks i.e. water, CO_2 and NH_3 . Considerable amount of biomass i.e. sludge, are thus produced and must be disposed of.

Tertiary treatment processes are used only to eliminate materials which are not amenable to secondary treatment. A treatment method for wool scouring effluent has been developed, consisting of evaporation and incineration plant in combination with a biological plant [56]. The resulting condensates from the evaporation plant and the incineration residues are recycled so that the water, ammonia and scouring aids are returned to the production plant [57].

Organic removal processes are achieved by adsorption, foam separation and chemical oxidation. In adsorption activated carbon, silica gel, chitosan fibre, fullers earth etc. are used to absorb impurities from waste water. The sizes from the

textile effluents can be removed by bioelimination i.e. adsorption by sludge. Acrylic acid and polyacrylate sizes can be readily disposed of by adsorption by the sludge. CMC cannot be eliminated in water treatment plants, whether by biodegradation, adsorption on the sludge or precipitation. Foam separation treatment involves the passing of compressed air through the waste water containing surface active agents and the foam rich in surfactant is separated. Chemical oxidation is used for decreasing the BOD. Ozone, H_2O_2 , manganese perchlorate are generally used for this purpose.

Inorganic removal processes are achieved by anerobic denitrification, algae harvesting, electro dialysis, ion-exchange resins, solvent extraction etc. The electrochemical technology is very effective in the reduction of colour. Ozone treatment is also applied primarily for discolouration, but it can also improve the quality of effluent in many other ways. Gamma radiation-induced oxidation appears to be effective in discolouring refractory dyes. Freezing, ammonia stripping, distillation are also employed to remove impurities from effluents.

The recovery of caustic from the mercerization process is a common practice in the textile industry. Mercerizer rinse water is normally recovered when its concentration is above 2-3% and below this concentration it is discharged to waste treatment. An alternative to this procedure is to use an ultrafiltration membrane to filter caustic rinse water before the solution goes to the evaporator. A flow sheet diagram of caustic recovery solution is shown in Fig. 13-12. The clarified and concentrated solution is then ready for re-use and consumption of caustic is significantly decreased [59].

The recovery of sizing agents by means of ultrafiltration has become very popular as a result of environmental legislation [59-61]. The recovery of chemicals, energy and water for reuse is more economical today. Recovery of PVA was one of the first recycle processes to be used by textile industry [62]. A diagram of PVA recovery system is shown in Fig. 13-13. An important factor is that when size is recovered, 60,000 gallons of discharge from each range per day is eliminated from the waste stream.

Hyperfiltration or reverse osmosis is a separation process involving the filtration of aqueous solutions by membranes capable of removing not only suspended particles but also substantial fractions of dissolved impurities, including organic

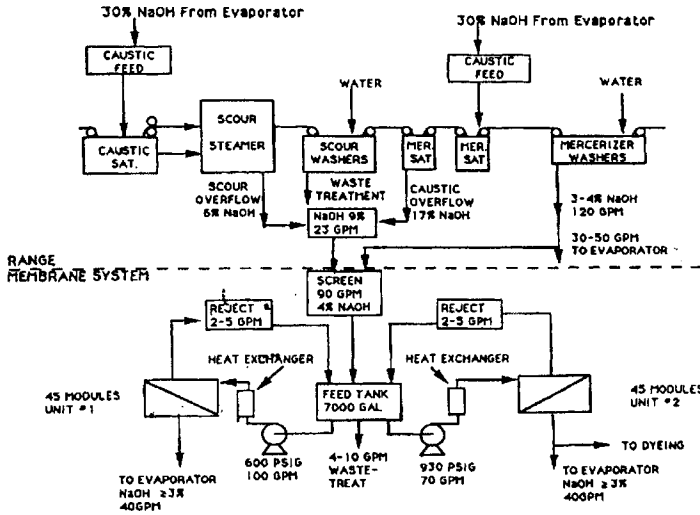


Figure 13-12. Caustic recovery system [58].

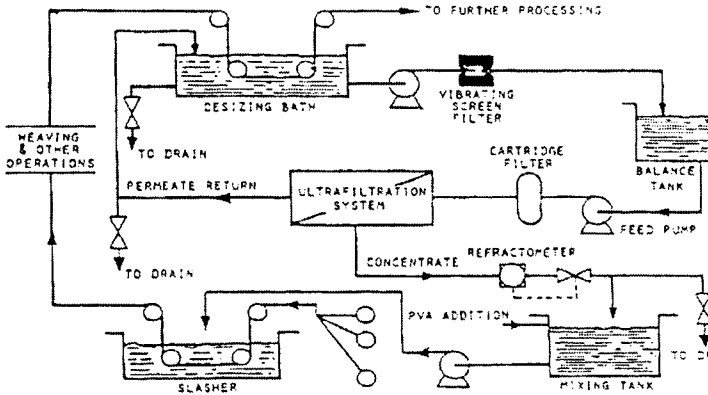


Figure 13-13. PVA recovery system [63].

and inorganic material. The use of reverse osmosis alone or in combination with other treatment is suggested for recovery of sizes [64-66]. In this method, water and soluble salts are selectively removed from the desizing liquor by passing it through ultrafiltration membrane. This is a system for making sizing agents more concentrated and recycle the reclaimed liquor in a continuous cycle during sizing and weaving. Fig. 13-14 shows a simplified line diagram of a system of making sizing agents more concentrated. With ultrafiltration, the membranes, which may

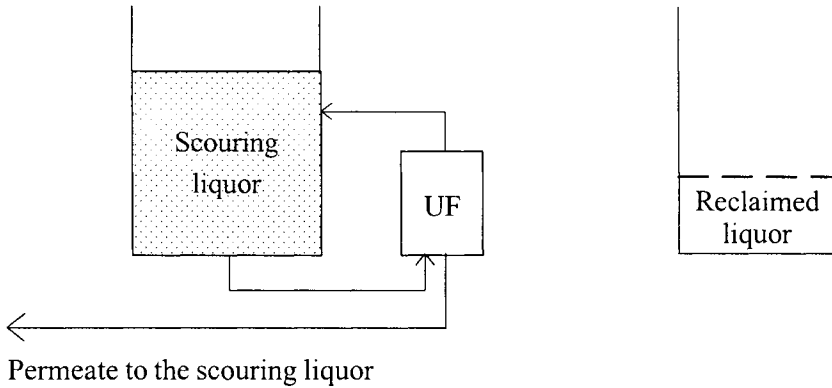


Figure 13-14. Increasing the concentration of sizing agent [66].

either be in the shape of tube or coil, retain the removed substances from a certain molecule size onwards. Technical details on ultrafiltration is presented in Table 13.16. An average permeation rate of 20-25 l/m²h is attained in increasing the con-

TABLE 13.16

Recycling Sizes by Ultrafiltration [67].

Initial concentration (%)	1.5
Final concentration (%)	8.1
Permeation rate	
Initial (l/m ² h)	130-150
Final (l/m ² h)	8-10
Average (l/m ² h)	20-25
Retentivity (%)	95
Temperature (°C)	80

centration of acrylic acid base size in washing liquors to a value of about 9%. With ultrafiltration the size containing scouring liquor is circulated until the cycle liquor reaches a desired concentration [68]. The regenerated size is reused per se or mixed with original product (10-20%). Recovery rates of 70-85% in recycling PVA sizes have been reported [69].

The recovery and reuse of size mixtures containing CMC, PVA, polyacrylates are studied by ultrafiltration technique [70]. Fig. 13-15 shows the extent to which different groups of sizing agents can be recycled. The influence extended by the

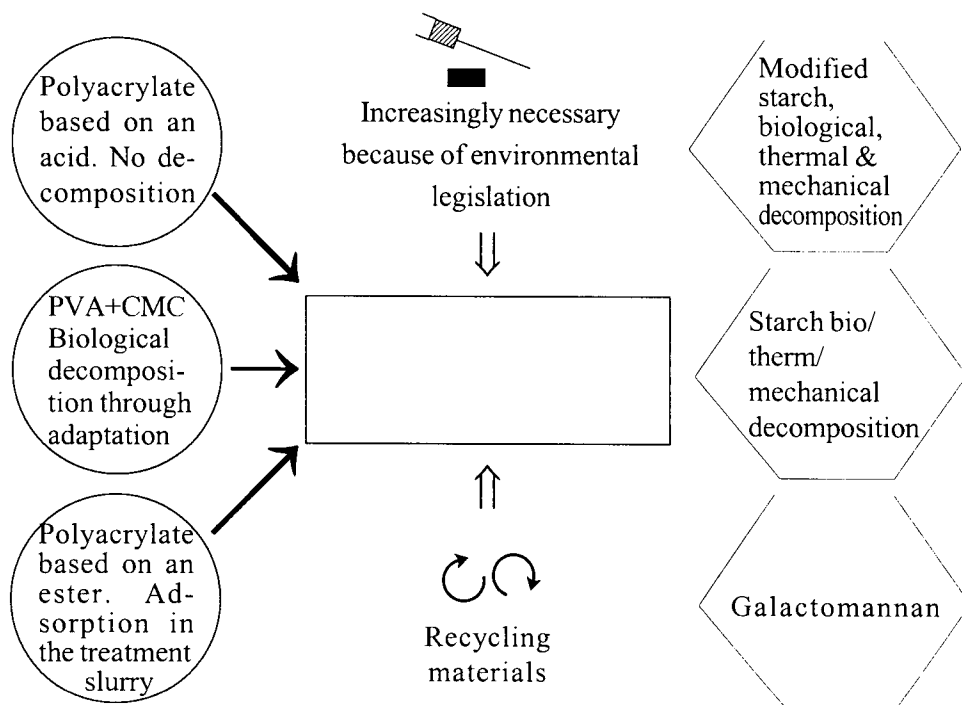


Figure 13-15. Recyclability of various groups of sizing agents [66].

salts commonly used (particularly Ca^{2+} ions), the thermal, mechanical and biological stability and the eliminability of these size mixtures are investigated [71]. It is found that size mixtures containing polyacrylate show marked advantages over mixtures of CMC and PVA. It is claimed that yarns sized with recycled liquor performed better during weaving than warp sized with the original liquor. This is because the short chain molecules are removed from the particular sizing agent during ultrafiltration. These are found again in the permeate. The improvement is the result of the size becoming more uniform. Modern techniques for recycling sizing agents are one way of reducing effluent loads in the textile industry. But the main difficulty is, the commission finisher has no reliable informations concerning the size content of the grey fabrics he has to finish [72, 73].

Every effluent treatment plant will produce solid waste, which has to be disposed off properly, as it contains hazardous chemicals. Some of these materials are highly toxic, others are corrosive, flammable, irritants, explosive, infectious etc. Disposal of these solid wastes always presents a problem. Waste disposal systems

commonly practised are landfill either on site or to municipal operation, incineration, ocean dumping, spray irrigation or hauling to municipal treatment plant. Most of the countries have approved landfills for various types of wastes with proper precautions. The incineration of textile waste is not usually recommended due to air pollution and the ash which has high concentration of heavy metals.

13.10 Protective Measures for Ultraviolet Radiation

The problems of ozone depletion in the upper atmosphere have led to increased problems of exposure of the skin to solar ultraviolet radiation [74]. Ultraviolet radiation to earth, due to the above effect could gradually affect human's immune system. Ailments like cataract, lung diseases and skin cancer would increase. Approximately 90% of non-melanoma and 65% of melanoma skin cancers have been attributed to ultraviolet exposure.

The UVR band has been identified as consisting of three regions, namely, UVA from 320 nm to 400 nm, UVB region from 290 nm to 320 nm and UVC from 200 nm to 290 nm. The regions of utmost concern for skin cancer are the UVB and UVA regions [75]. UVC, UVB and UVA radiation are usually absorbed by the ozone layer, with no UVC and only half of the UVB reaching the surface of the earth. The size and depth of the Antarctic ozone hole has caused concern particularly in Australia, where it has been suggested that a decrease of 1% in ozone would lead to increase in the ultraviolet radiation at the earth's surface and may eventually lead to a 2-3% increase in skin cancer [76].

Protection from UVR is available through the use of sunscreens and clothing. Sunscreen lotions contain UVR absorbers and sun blockers contain pigment that physically blocks UVR. Hats, sunscreens, sunglasses and clothing can be used to decrease the exposure to ultraviolet radiation by a factor of 10 or more, as well as by people avoiding exposure to the sun at its maximum [74].

This opens up another area of opportunity for textile fabric and garment producers to manufacture comfortable ranges of clothing for leisure and for outdoor workwear that offer significant enhanced protection against ultraviolet radiation. The appropriate selection of dyes, fluorescent brightening agents, and particularly UVR absorbers should enable cotton finishers to provide the high levels of protection demanded [77, 78]. The importance of assessing the protection afforded by apparel fabrics is recognised and there is much research being conducted on the

manner in which different fibres, fabrics, fabric construction, colorants, additives, etc. influence the UV protection of textiles [79-82]. The cover factor of a fabric (the percent of open spaces to closed spaces) has been identified as an important determinant in protectiveness against UVR transmission and SPF (sun protective factor) [83]. Sun protection factor (SPF) of fabrics is improved by applying UV absorbers to fabrics [81]. Woven fabrics usually have higher cover factors than knit due to the yarns in woven fabrics lying closely together and minimising spaces between the yarns and thus the application of a reactive UV absorber performance depends on the fabric [84]. Pale shaded fabrics of cotton, silk, polyamide show little protection against intense UV radiation. The darker shade of any colour shows higher protection provided from sunburn [80].

Two additional considerations in evaluating textiles as protection from UVR are wetting and stretching. It is shown that the SPF of fabrics is reduced when the fabrics are wet [84, 85]. A decrease in SPF values of fabrics as a function of stretching of fabrics is observed [85, 86].

SPF is the ratio of the length of time of solar radiation exposure required for the skin to show redness (erythema) with and without protection. The term SPF or UPF (ultraviolet protection factor) has been introduced such that a garment of UPF 15 will provide the same amount of protection against solar ultraviolet radiation as a sunscreen of SPF 15. Garments with a UPF value of 20-29 offer high protection (UVR transmission 5.0-3.3%). A UPF value of 30-40 (UVR transmission 3.3-2.5%) offers very high protection and a UPF value of 40 + offers maximum protection with a UVR transmission of 2.5%.

The protectiveness that fabrics and garments can afford against UVR is of great importance to consumer throughout the world and a systematic research is yet to be performed on each of the variables that has been identified as impacting on SPF of fabrics.

REFERENCES

- 1 G. Durig, *Rev. Prog. Color.*, 7 (1976) 70.
- 2 J. Carbonell, H. Egili and M. Perriy, *Amer. Dyestuff Rep.*, 66 (8) (1976) 44.
- 3 B. P. Jhala and S. R. Bhatt, *J. Text. Assocn.*, (May 1995) 33.

- 4 H. A. Shah, R. V. Tiwari and P. K. Trivedi, *Colourage* (Dec 1987) 19.
- 5 H. C. Speil and W. K. Schwartz, *Textile Chemicals and Auxiliaries*, Reinhold, New York, NY, (1957) p 201.
- 6 W. W. Stickney and T. M. Fosberg, *Treating Chemical Wastes by Evaporation*. *Chemical Engineering Progress*, 72 (1976) 41.
- 7 M. E. Bessing, ASME Paper No. 79-Sol. 23 (1979).
- 8 ERDA Final report, CDRL/PA 10 (1977).
- 9 G. R. Pillai et al., *Indian Textile J.*, 93 (12) (1983) 53.
- 10 M. D. Dixit, *Engineering Design*, 11 (1982) 42.
- 11 M. L. Gulrajani and S. G. Gupta, *J. Soc. Dyers Colourists*, 106 (1990) 98.
- 12 *Textile Asia*, 10 (8) (Aug 1979) 92.
- 13 *Textile Asia*, 8 (9) (1977) 146.
- 14 *Textile Asia*, 10 (8) (Aug 1979) 80.
- 15 *Modern Textiles*, 58 (2) (1977) 12.
- 16 *Textile Progress*, 14 (2) (1986) 19.
- 17 David Gross, *Knitting Times*, 46 (23)(1977) 13.
- 18 *Modern Textiles*, 58 (2)(1977) 10.
- 19 *Amer. Dyestuff Rep.*, 63 (7) (1974) 34.
- 20 *Textile Month* (Dec 1975) 65.
- 21 K. Ranaszeder, *Melliand Textilberichte*, 73 (4) (1992) E 169.
- 22 E. Brenner, *Melliand Textilberichte*, 75 (1994) 742.
- 23 ATIRA Research Note, CCT/61, 2 (July 1961).
- 24 *Chem. Engg. News*, 15 (Oct 1975).
- 25 S. Switer and Simpson, *Amer. Dyestuff Rep.*, 61 (5) (1972) 35.
- 26 J. Ballard, *Teintex*, 44 (4/7) (1979) 13.
- 27 C. Duckworth and J. J. Thawites, *J. Soc. Dyers Colourists*, 85 (6) (1969) 225.
- 28 *Textile World*, 130 (1980) 27.
- 29 W. B. Achwal, *Colourage*, 37 (Sept 1990) 40.
- 30 J. M. Marzinoveski, *Textilveredlung*, 28 (1994) 154.
- 31 *Textile Dyer and Printer*, 28 (Nov 1995) 18.
- 32 James Robinson Ltd., *J. Soc. Dyers Colourists*, 111 (June 1995) 17.
- 33 Harald Dunser, *The Indian Textile J.*, 102 (4) (1992) 80.
- 34 S. Durig., *Rev. Prog. Color.*, 7 (1976) 70.

- 35 D. S. Bajpai and R. C. Kausik, *Synthetic Fibres* (Apr/June 1990) 7.
- 36 S. D. Cooper, *The Textile Industry, Environment Control and Energy Conservation*, Noys Data Corpn., USA (1978) 210.
- 37 J. Janitza, S. Koscielski and A. Krauter, *Textil Praxis*, 49 (1994) 61, 168, 226.
- 38 R. H. Souther, *Amer. Dyestuff Rep.*, 58 (1969) 13.
- 39 R. H. Souther, *Amer. Dyestuff Rep.*, 55 (1966) 685.
- 40 J. J. Porter, W. F. Nelan and A. R. Abenathy, *Chemical Engg. Symposium Series, Water*, 67 (1970) No. 107.
- 41 Mann and Reid, *J. Amer. Oil Chem. Soc.*, 48 (1971) 794.
- 42 R. B. LeBlanc, *Amer. Dyestuff Rep.*, 56 (1967) 623.
- 43 H. J. Ross and N. F. Crowder, *J. Textile Inst.*, 50 (1959) 274, 320.
- 44 R. Hoffman and G. Trimmer, *Melliand Textilberichte*, 75 (1994) 831.
- 45 F. Conzelmann, P. Würster and Z. Zahn, *Textil Praxis Int.*, (1989) 144.
- 46 G. Schulz, *Textil Praxis Int.*, 1 (1990) 40.
- 47 H. Bachus, *Textilveredlung*, 30 (1995) 152.
- 48 R. C. Bettrille, *AATCC Int. Conf. Book of papers*, 1993, p 205 & 214.
- 49 P. Würster, *Textil Praxis*, 47 (1992) 960.
- 50 R. Anilker, *Rev. Prog. Color and Rel. Topics*, 8 (1977) 60.
- 51 P. I. Norman and R. Seddon, *J. Soc. Dyers Colourists*, 107 (1991) 216.
- 52 R. H. Leary, *Textile Asia*, 11 (10) (1980) 118.
- 53 A. Schwarzmuller, *Amer. Dyestuff Rep.*, 77 (4) (1988) 32.
- 54 N. Atharasopoulous, *Melliand Textilberichte*, 73 (4) (1992) E 167.
- 55 R. P. Mathew, *Amer. Dyestuff Rep.*, 63 (8) (1974) 19.
- 56 R. Hoffman and G. Timmer, *Melliand Textilberichte*, 75 (1994) 831.
- 57 R. H. Hoffman and G. Timmer, *Melliand Textilberichte*, 72 (1991) 562.
- 58 J. L. Gaddis, H. G. Spencer and P. A. Jermigan, *Advance in RO and UF*, American Chemical Society Meeting, Toronto, Canada, June 1988.
- 59 L. Johnson and T. W. Wett, *Chemical Processing*, (March 1980) 36.
- 60 J. Troutner et al., *Textil Praxis*, 48 (Sept 1993) 697.
- 61 L. S. Meyer – Stork, *Melliand Textilberichte*, 75 (1994) 828.
- 62 C. W. Aurich, *Recovery by Filtration*, AATCC Symposium, *Textile Technology/Ecology Interface*, Charlotte, N. C, May 1975.
- 63 C. R. Hoffman, *J. Coated Fabrics*, 10 (Jan 1981) 178.

- 64 J. J. Peter and T. N. Sargent, *Textile Chem. Color.*, 9 (11) (1977) 38.
- 65 Dittrich, *Melliand Textilberichte*, 54 (1973) 853.
- 66 J. Langer, *Melliand Textilberichte*, 75 (1994) 804.
- 67 H. Leitner, *Melliand Textilberichte*, 75 (10) (1994) 807.
- 68 O. Deschler, *Melliand Textilberichte*, 60 (1980) 42.
- 69 G. D. Robinson, *Textile Asia*, 24 (2) (1993) 58.
- 70 M. Diehl and W. Schindler, *Melliand Textilberichte*, 76 (1995) 129.
- 71 J. Langer, *Melliand Textilberichte*, 76 (1995) 134.
- 72 F. Thater, *Chemiefasern/Textilind.*, 22/74 (1972) 659.
- 73 F. Thater, *Textil Praxis Int.*, 29 (1974) 1210.
- 74 J. M. Caldwell and A. E. Mizusawa, *Proc. 6th Int. Conf. on Textile Coating and Laminating*, Dusseldorf, Germany, 1 (Nov 4-5, 1996).
- 75 T. A. Perenich, *Colourage*, Annual (1998) 71.
- 76 I. Holme, *Colourage*, Annual (1998) 41.
- 77 R. L. Shishoo, *Proc. 6th Int. Conf. on Textile Coating and Laminating*, Dusseldorf, Germany, 1 (Nov 4-5, 1996).
- 78 A. H. Luiken, *Redtech Europe Conference*, (1989) 207, Florence.
- 79 M. Pailthorpe, *Proc. Textiles and Sun Protection Mini Conf.*, 1993, pp 32-50.
- 80 H. P. Gies et al., *Health Physics*, 67 (2) (1994) 131.
- 81 R. Hilfiker et al., *Textile Res. J.*, 66 (1996) 61.
- 82 G. Reinert et al., *Textile Chem. Color.*, 29 (12) (1997) 36.
- 83 R. Hatch et al., *Family and Consumer Sciences Res. J.*, 23 (1994) 198.
- 84 A. P. Jevtic, *Australian J. of Dermatology*, 21 (1990) 5.
- 85 D. G. Sanford et al., *Medical J. of Australia* 62 (1995) 422.
- 86 R. M. Sayre and S. N. G. Hughes, *Skin Cancer J.*, 8 (1993) 41.

PRE-TREATMENT OF TEXTILES UNDER PLASMA CONDITIONS

14.1 Introduction

To - date, the required surface modification of the fibre is mainly accomplished by wet chemical processes. An appropriate alternative to its conventional techniques is given by the pre-treatment of textile fibres with low temperature glow-discharge plasma in air [1-10]. There is also an increase in patent applications on the latest developments in plasma technology [11-14]. Physico-chemical method of modifying the surface of polymer substrates without changing the nature of the bulk of the substrate has been of great interest. Particularly in the area of pre-treatment of textiles, this technology which is relatively new to the textile industry, seems to bring about obvious advantages in relation to the conventional technique. The reason for this interest is the intriguing possibility of modifying polymers and obtaining new and interesting properties leading to better performance.

Conventional wet pre-treatment processes of textiles are generally energy consuming process. Plasma modification of textiles saves large quantity of water, chemicals, and electrical energy. Ecological and economical constraints which are imposed on the textile industry to an increasing extent, call for the development of environmentally friendly and economic finishing processes. Large savings are possible since the plasma process does not produce large volumes of waste or toxic by-products [9].

14.2 The Concept of plasma

Plasma is known as the fourth state of the matter. Plasma is partially ionised gases, consisting of ions, electrons and neutral particles. These gases are produced by electrical discharges. The plasma state has played a key role in the evolution of life on earth and holds a great potential for future. Apart from the process of nitrogen fixation which goes on year after years during thundering of clouds, lightning and the rains, it is believed that the first “live” molecule namely the amino acids were synthesized under the conditions of plasma. During the primitive days of earth, nitrogen and hydrogen combined to produce ammonia, then coupled it to methane and carbon dioxide to synthesize amino acids. In spite of such a long history, the phenomenon of electrical discharges has been used for polymer modi-

fications over the last thirty years or so [15-17]. Particular mention may be made of pioneering work done by Goodman [18], Kassenbeck [19], Pavlath [20], Split [21] and others [22,23], for polymers.

Generally speaking there are various forms of an electrical discharge which differ in their external appearance and the temperature, depending on the pressure and the voltage source connected to the gas section. This current flow is brought about by ionisation through a gas, whereby the current flow is produced by applying high voltages. For textile fields of application, fundamentally only "cold" plasma and in particular the corona and glow-discharge are of interest. "Cold plasma" are unbalanced plasma or low temperature plasma. The electron energy is up to 100 times greater than the energy of the gas particles. "Hot plasma" are known from nuclear fusion. The energy of electrons and gas particles is equal.

14.2.1 Corona discharge

This is generated at gas pressures equal to or near to the atmospheric pressure with an electromagnetic field at high voltage (>15 kV) and frequency in the 20-40 kHz range for most practical applications today. It develops when a high voltage is applied to electrodes, but the ignition of a spark between them is prevented by an insulator. In order to trigger a corona discharge, a high field strength must be produced at one electrode. Through high voltage, the electrons are accelerated in the direction of the insulator. The insulator is situated directly under the substrate to be treated. On their way to the substrate, the electrons collide with air molecules and form ozone and nitric oxides in the process. The electrons which reach the substrate are due to their high energy (approx. 5eV) and able to split covalent linkages. In doing so, radicals are created on the fibre surface which react with ozone or nitric oxides, i.e. the fibre surface is being oxidised and thereby becomes more polarized.

14.2.2 Glow - discharge

This is generated at gas pressures in the 0.1-10 MPa range with an electromagnetic field in a lower voltage range (i.e. 0.4-8.0 kV) and a very broad frequency range (0-2.45 GHz). Glow-discharge has found practical use in fluorescent tubes. A glow - discharge is brought about when an increased voltage is applied to two electrodes which are spatially separated in a container with reduced pressure (approx. 10^{-3} - 10^{-4} bar). Due to the possibility of feeding in different gases, the surface of a

substrate to be treated can be modified in a chemically specific manner.

Both forms of discharges are regarded as a 'low temperature plasma', but the term 'plasma' is used to describe the glow-discharge only. Corona discharges are generally suitable for flat products and subsequent processing is done immediately after the treatment. In contrast to corona discharge, the electrons produced in the glow-discharge are of high energy, as they are not slowed down by colliding with air molecules (corona discharges originate in an air atmosphere). Glow-discharges are suitable for all kinds of textile products and their efficiency does depend on the time elapsed between the treatment and further processing. The electrons having been created in glow-discharge can also better penetrate the fibre surface and thereby also alter the fibre surface more intensively.

Uneven finishes cannot be ruled out in the case of dense and heavy fabrics. In heavy fabric, for instance, the water contents at the cross-over points of the individual yarns are very high, while non-overlapping areas of the yarns have relatively low moisture contents. The same applies to the individual fibres in the yarn structure. As the conductivity of the wool being an insulator in its dry state, increases with its moisture content, greater voltage gradients may occur in the "fibre-free areas" than at the cross-over points of the fibres and yarns respectively during a corona discharge. This does not apply to fabrics of low fibre density, as here no such large moisture differences occur within the fabric structure and thus corona treatment is the method to be chosen. It can be applied in a more cost-effective manner than the glow-discharge which must be carried out in a vacuum. An even treatment of fabrics having high weights of surface or of combed sliver, however, is only possible with the aid of the glow-discharge. The pressure reduction in the treatment chamber being necessary for the production and maintenance of the plasma, leads to drying of the material and thereby to the equilisation of moisture differences. In addition to that a homogeneously distributed "plasma cloud" also develops between the individual fibres which allows an even treatment in the dense fabric structure.

14.3 Generation of Plasma and its Action

Plasma may be produced by :

- (i) thermal ionisation at high temperatures at normal gas pressures, or

(ii) by using electrical discharges-the frequency of the electrical energy vary from zero (d.c.) to 10^{11} Hertz (microwaves).

These may be subdivided as : (a) electrode discharges (glow, plane, point, corona etc.) and (b) electrodeless discharge using radio frequency (RF) at low gas pressures. The use of RF has a further advantage that it can be used to bring about RF heating. Various types of electrode assemblies can be used for initiating plasma.

14.3.1 Machine performance for producing plasma

The field of industrial plasma engineering has grown in recent years. The uses are motivated by plasma's ability to accomplish industrially relevant results more efficiently and cheaply than competing processes. The research program concerning plasma treatment of textile materials was launched at the Polish Textile Institute in 1973 to improve the soil release properties of double jersey fabrics from texturised polyester yarns. The first experiments with wool date back to 1980 to replace the chlorination in fabric preparation for printing. Three machines for continuous plasma treatment of wool top have been developed as follows :

- 1983 First laboratory device with capacity of ~ 2kg/h
- 1986 First machine with capacity of ~ 20 kg/h
- 1992 First machine with capacity of ~ 40 kg/h.

For example, the shrink proofing of wool using corona discharge has already reached a stage of commercial production [24].

It is necessary to recognise the difference between polymer forming plasmas and non-polymer forming plasmas in order to understand the true meaning of the processing factors of glow-discharge polymerisation. Not all glow-discharges yield polymer deposition. Plasmas of Ar, Ne, O₂, N₂ and air are typical non-polymer forming plasmas. In case of polymer forming plasmas there is pressure change that occurs before, during and after the glow-discharge. In the other case no pressure change occurs. Although a number of methods can be used to generate plasma, the methods utilised in surface modification of textiles are more or less limited to some kind of electric discharge. The volume of glow-discharge as well as intensity of glow are highly dependent on the mode of discharge, the discharge power and pressure of the system. The chamber where the polymer is modified is known as the reactor. The volume and intensity will affect the rate of polymer modification, depending on the geometric factors of the reactor. Electric discharge can be obtained

in number of ways and numerous combinations of factors are involved in the design of reaction vessel. The type of electric power source and mode of coupling also play an important role. Based on this R.F., low frequency or D.C. source can be used for excitation and coupling can be either inductive or capacitive.

Figs. 14-1 to 14-5 describe the typical reactors of different kinds for producing plasma. The description given in the caption is self-explanatory. Fig. 14-1 shows

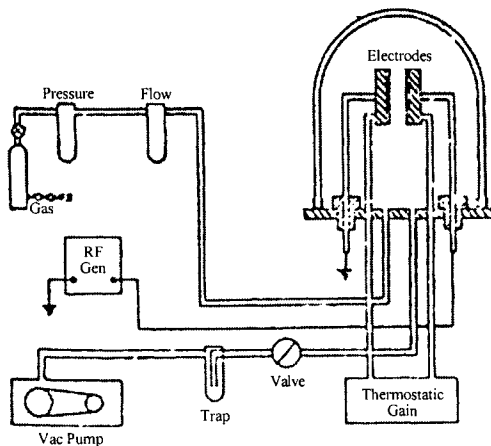


Figure 14-1. Typical laboratory equipment for glow-discharge experiments [25].

the schematic representation of glow-discharge reactor with internal electrodes. The two copper electrodes in the glow-discharge chambers are 1 cm apart and the fabric samples are held rigidly between these electrodes. Power is supplied by 500-W 3.14 MHz generator. The chamber is evacuated to 10^{-3} torr and if required monomer is then introduced at the ambient temperature, its pressure and flow being regulated by valves.

Fig. 14-2 shows the experimental arrangement that is necessary to be made for producing plasma. It consists of a cylindrical glass chamber having arrangements for connecting to vacuum pump, an inlet and outlet for gas and an inlet to introduce monomer for the purpose of grafting experiments. A radio frequency oscillator, operating at 18 MHz can be used as a source to produce electrodeless discharge. The power output can be varied from 100 to 250 watts. The gas pressure inside the tube may be maintained at about 0.1 mm of Hg. A special glass holder is designed to introduce the sample into the plasma chamber. The samples are subjected to plasma treatment for various durations of time. Occasionally a D.C. power supply

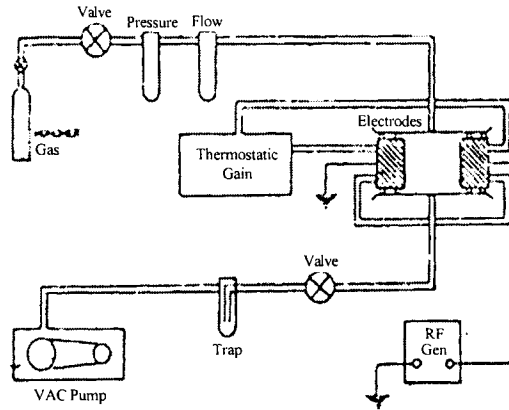


Figure 14-2. Schematic representation of a glow-discharge reactor with internal electrodes

operating between 400 -2000 volts is used to produce gas discharge.

Fig. 14-3 shows schematic representation of glow-discharge reactor with exter-

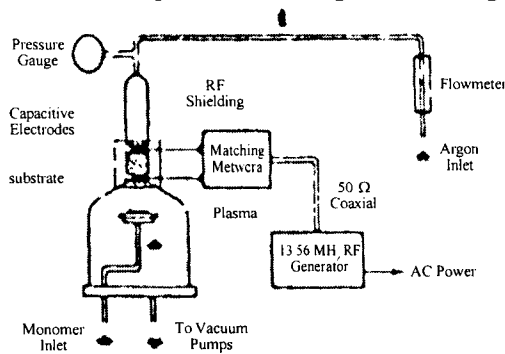


Figure 14-3. Glow-discharge reactor with external electrodes.

nal electrodes. A substrate is placed in the tall frame portion. Figs. 14-4 and 14-5 show the schematic representation of corona reactors. Fig. 14-5 shows the corona reactor with a rotating drum on which substrate is placed. The type and rate of polymer formation depend very much on the type of reactor.

The practical advantages of textile plasma exposure have been documented by Rakowski [9], who compared conventional chlorination process with a new process based on the exposure of wool to a low pressure plasma using the apparatus shown schematically in Fig. 14-6. Wool tow is fed continuously into a vacuum

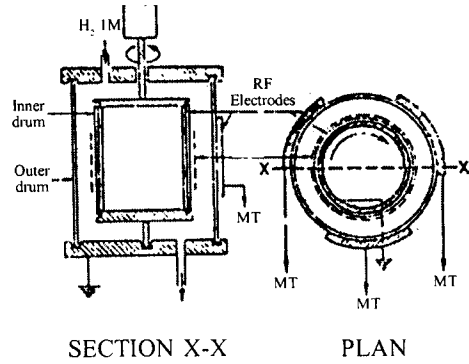
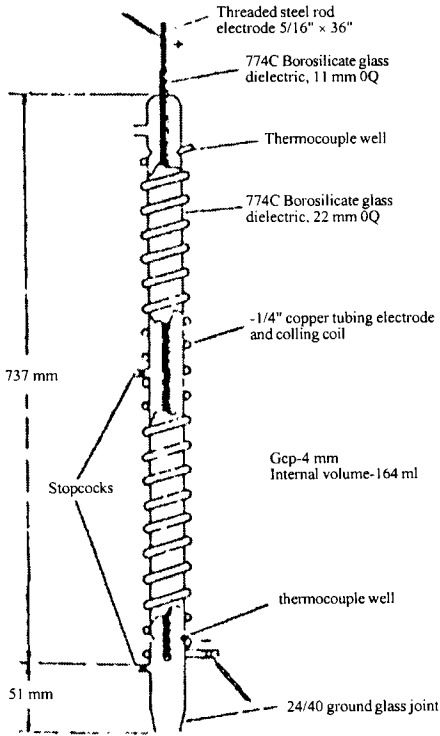


Figure 14-4. Schematic representation of corona reactor.

Figure 14-5. Schematic representation of corona reactor with a rotating drum on which the substrate is placed.

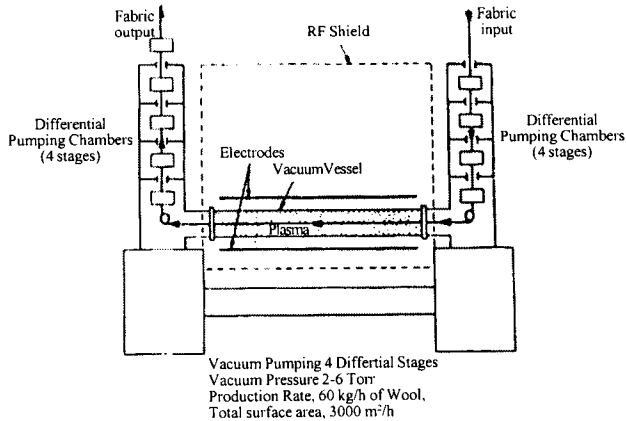


Figure 14-6. Apparatus for low pressure plasma treatment of wool [9].

chamber operating at pressures of 2 to 6 torr, where a glow-discharge plasma provides active species to which the wool is exposed. A novel feature of this approach

is the continuous feeding of the wool tow into and out of the vacuum system through several differential stages of vacuum pumping.

More recently, a group affiliated with Sofia University in Japan [26-28] has reported the generation of both filamentary and glow-discharge plasmas at one atmosphere of pressure in such gases as helium, and argon with an admixture of acetone. Similar work is also originated independently in the UTK Plasma Science Laboratory at the University of Tennessee in Knoxville [29-34]. A schematic diagram of the one-atmosphere glow-discharge plasma reactor system developed at the UTK Plasma Science Laboratory is shown in Fig. 14-7. The reactor volume is

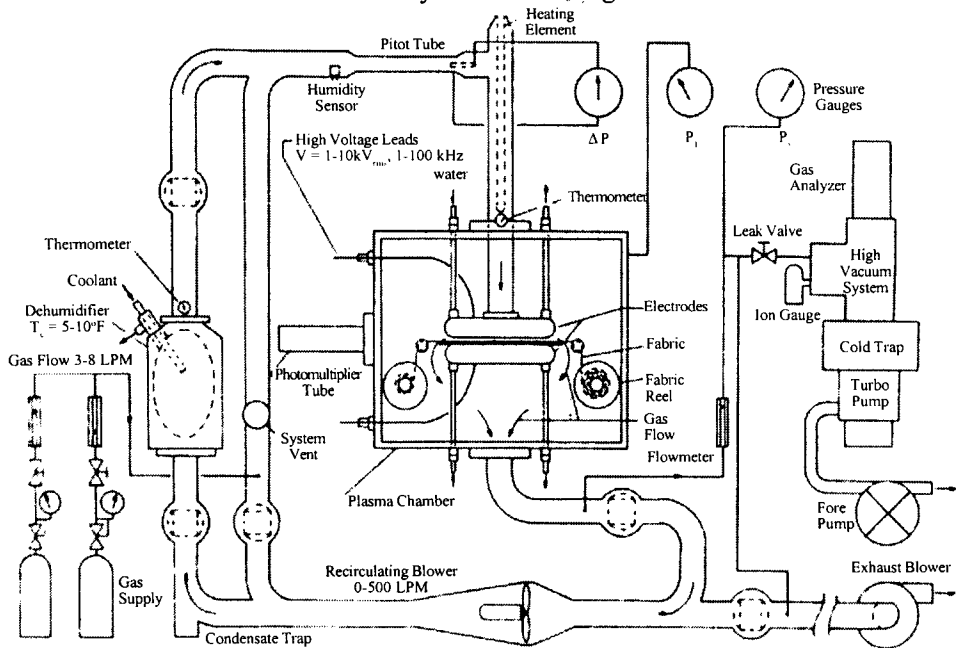


Figure 14-7. Schematic drawing of the one-atmosphere glow-discharge plasma reactor [35].

bounded by two plane, parallel plates across which a kilohertz electric field is imposed. The electric fields must be strong enough to electrically break down the gas used, and are much lower for helium and argon than for atmospheric air. The parallel face electrodes constituting the discharge region are placed in a Plexiglas enclosure. The working gas is recirculated and chilled to remove moisture, and reheated as required. The lower electrode has a solid stainless steel face and is covered with a 3.2 millimeter thick Pyrex insulating plate. The upper electrode has a perforated face of stainless steel with 650 holes 3.2 millimeter in diameter. Gas

flow is introduced on the back side of this electrode and flows downward through the perforated face of the electrode. Fig. 14-8 is a schematic diagram of the upper

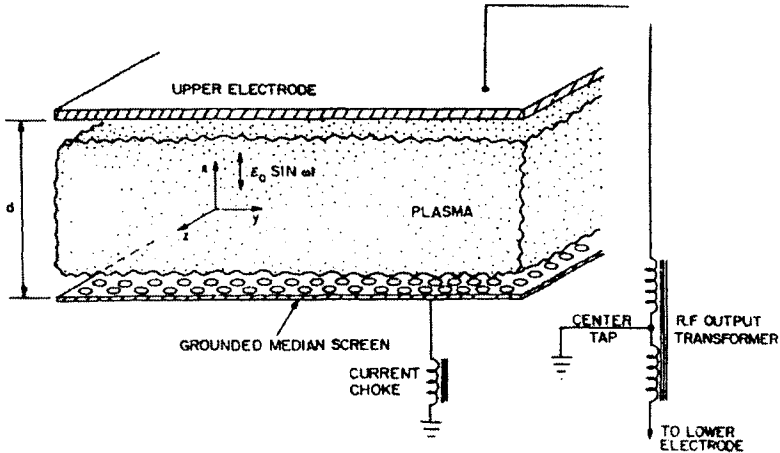


Figure 14-8. Electric field of a radio frequency power between upper and grounded midplane electrodes [35].

chamber of one-atmosphere glow-discharge plasma reactor. The lower boundary of this space is the midplane screen, the floating potential of which should remain near ground if the power supply output is connected as a push-pull circuit to the two electrodes with a grounded center tap. This reactor does not require any vacuum system, and only a simple enclosure is needed if one wishes to operate with gases other than atmospheric air.

The discontinuous (batch) machine (Fig. 14-9) for fabric treatment developed

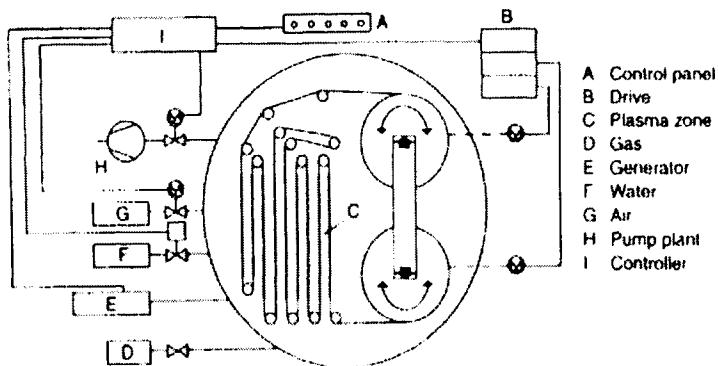


Figure 14-9. Batch plasma machine KPR-180 for fabric treatment [36].

by the Tecnoplasma SA consortium in Switzerland, based on research and construction work performed in Niekmi, Russia, for the last 16 years, has recently become available as production equipment.

The most recent machine for continuous plasma treatment of wool top developed at the Textile Institute in Łódź consists of (Fig. 14-10) a vacuum generation

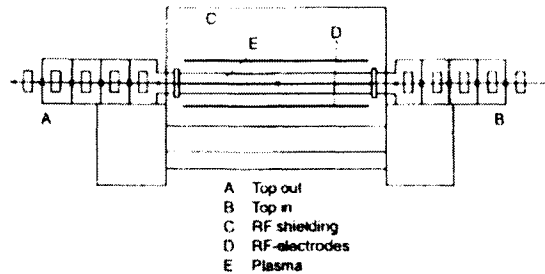


Figure 14-10. Prototype machine for continuous plasma treatment of wool top [36]. unit, a plasma generation unit, a top transport and collecting system. The glow-discharge is generated in a 45.8 litres processing chamber at 13.56 MHz and average RF energy density of 0.12 W/cm^3 , provided that there is good coupling of the RF generator and plasma generation circuit. The machine capacity is estimated as $\sim 40 \text{ kg/h}$.

14.3.2 The interaction of plasma with substrate

The interaction of plasma with materials can be roughly divided into three different classes [37] :

- (i) Reactions due to formation of ions which would lead directly to a new chemical product like formation of NH_3 , NO_2 , ozonisation etc.
- (ii) The second type of plasma reaction is the initiation of polymerisation i.e. deposition of thin uniform polymer film on the electrodes. Organic monomers in the vapour phase, like other gases, are ionised by bombardment of electrons under the discharge conditions. Such ions when neutralised have energy which leads of rapid polymerisation. Films having good stability, insulating properties, free of holes and uniform thickness can be obtained at a rate of few grams per kwh. Continuous movement of textiles, paper etc. through flat plate electrodes (0.1 m separation) for coating is possible. Manufacturing of thin film for capacitors, coating of cans or metal surfaces has been achieved.

- (iii) The third type of plasma reaction is concerned with effects produced at organic polymer surfaces in contact with plasma. This type of reaction forms the basis of major developmental work on textiles. The energetic ions from the plasma break organic bonds with the evolution of gaseous products (for e.g. hydrogen from hydrocarbons) and the formation of carbon free radicals. These radicals can in turn lead to chemical reactions at the surface of the substrate [38,39].

The essential plasma processes are presented in Fig. 14-11. The process which

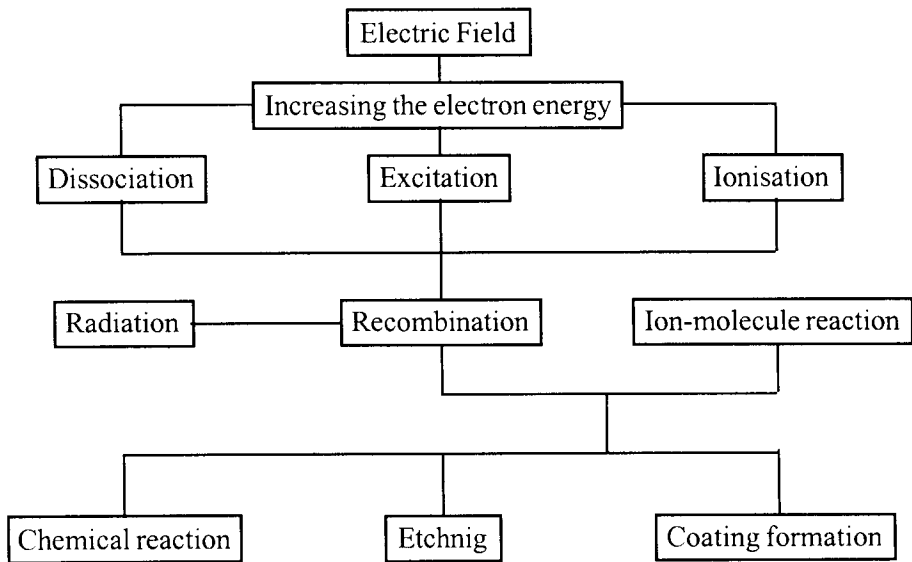


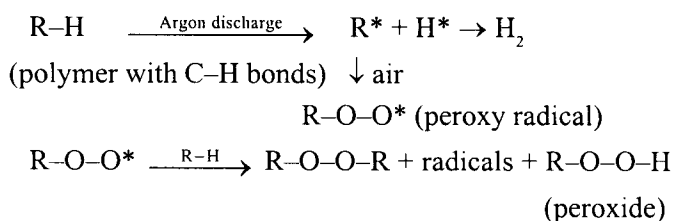
Figure 14-11. Basic process in plasma (Courtesy of Amann und Söhne GmbH).

can occur are cross-linking, solid-state polymerisation, etching action, radical formation and degradation. Which of these processes are predominant, however, strongly depend on the nature of gas, pressure and the power used for the glow-discharge. These reactions may be discussed under separate categories.

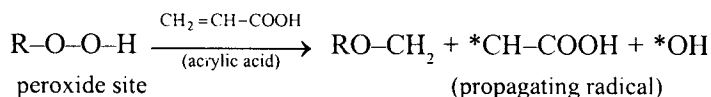
Recombination : When the rate of producing surface radicals is high and air is excluded, a tough cross-linked shell is formed that can offer protection against solvent attack, penetration by vapours or ions in solution or thermal disorientation. This type of surface cross-linking can be useful for : (a) limiting of plasticizer loss and extending the life of polyvinyl chloride tiles or other plasticized products, (b) rendering water soluble products like polyvinyl pyrrolidene partially water resistant for time delay encapsulation.

Oxidation, Oxidative degradation : In oxygen containing plasma, surface excitation leads to absorption of oxygen and formation of polar surface of ketone, hydroxyl, ether, peroxide and carboxylic acid groups that are much more hydrophilic (wettable) than the untreated surface. Thus articles like flannel, polypropylene non-woven fabrics, PE film, and Teflon have shown marked increase in wettability after exposure to air discharge. Corona discharge treatment is routinely applied to PE film to make it printable. Plasma treatment can also lead to improved adhesion properties (through mechanism discussed below).

Peroxide formation : A high proportion of reactive sites is converted to peroxide form when a typical textile or plastic substrate is exposed to Argon plasma and then to air. If R-H represents carbon-hydrogen bonds susceptible to the dissociation by exposure to plasma, then

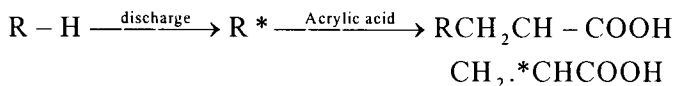


Since peroxides are known to act as initiators for vinyl polymerisation, it follows that under suitable conditions a vinyl monomer will react with peroxide group to produce a graft copolymer with the substrate, e.g.



Since peroxide groups are indefinitely stable under ambient conditions and thus, they can be stored as reactive sites and used at a later time. These surfaces also show improved adhesion in different circumstances.

Initiation for grafting : The free radicals formed on the surface of fibre by exposure to plasma can be used directly to initiate polymerisation, with new polymer bonded firmly to the surface by carbon linkages. Thus, a new polymer can be applied in the following manner :



14.4 Surface Modification of Fabrics Under Plasma Treatment

The plasma-induced surface modification of textile substrates has gained increasing importance over the last few years [40]. Probably the most advantage behind this renewed interest in plasma technology is the restriction of the concentration of AOX compounds in the discharged effluents to 0.5 mg/l [41]. The other reason for this interest is the intriguing possibility of modifying properties leading to better performance. The range of applications is diverse and modifications of surface of various materials like cotton, wool, silk, polyester have been reported. Plasma treatment generally takes place in dry conditions, thus the fibres are not swollen. The changes in properties induced by plasma treatment are therefore restricted to the surface and any damage to the interior of the fibre is very unlikely. The physico-chemical nature of the modified fibre surface has a tremendous influence on the following important phenomenon:

- i) Static electricity build up and dissipation.
- ii) Moisture transport and comfort.
- iii) Oily stain adsorption and release in detergent solution.
- iv) Soil deposition, release and redeposition in detergent solutions.
- v) Wettability and adhesion.
- vi) Scourability and bleachability of textiles.
- vii) Wettability and dyeability

From the physical point of view, roughening of fibre surface as seen by atomic force microscopy is responsible for changes in the coefficient of friction, top cohesion, spinnability, yarn strength, etc., as well as for increase in felting resistance of wool. From the chemical point of view, the oxidation of the fibre surface and interaction with polymeric materials are the main factors responsible for improvements in various properties of plasma treated materials.

14.4.1 Plasma treatment of wool

The effects of a plasma treatment on wool such as anti-felting effect, degreasing, improved dyestuff absorption and increase in wetting properties have been documented in numerous publications [42-46]. Other changes in wool properties are summarised below :

- (i) Plasma treatment increases the fibre/fibre friction as measured by Röder method [47], but reduces the differential friction effect (DFE) as defined by Mercer [48] and Lindberg [49].

- (ii) Plasma treatment does not change the strength and elongation; the breaking force in loop form is slightly reduced.
- (iii) The plasma treatment increases the top cohesion by a factor of 1.5-2.0; this increased cohesion remains stable after prolonged storage.
- (iv) The specific electrical resistivity does not change considerably after plasma treatment.
- (v) The fatty matter content in wool is reduced by about one-third due to plasma treatment.
- (vi) The water content of the wool top is reduced by about 3% due to plasma treatment.
- (vii) There is changes in spinning behaviour of plasma treated wool [50,51]. The spinning aids applied on the first drawing frame are carefully selected. The rubbing intensity or twist of the slubbing should be increased. Reduction in breaks rate at ring spinning frame is usually observed and an increase in yarn tenacity by 20-25% is observed for all yarns.

The normal process of preparing light weight woollen fabrics has involved a chlorination operation. However, this leads to difficult working conditions, rapid corrosion of equipment and has a bad effect on the local ecology. Plasma treatment is a good alternative for chlorination treatment although two problems remain : namely the efficiency of plasma/polymer system itself and the ways and means to improve the fabric handle [52]. However, plasma treatment considerably reduces the felting potential for any product obtained from the modified wool. The reduction in the content of covalently bound highly hydrophobic methylicosanoic acid and increase in content of oxidised sulphur species are the main factors responsible for improvements in dyeing and shrinkproofing of plasma treated wool.

Plasma treatment of wool followed by polymer application has also been studied [36]. Almost all polymers used currently on pre-chlorinated wool cannot be used on plasma-treated top. Silicone resins applied to plasma-treated wool increase the shrinkage over that for untreated wool. However, the combined plasma/PMS/Hercosett treatment encompassing the top treatment gives excellent shrink resistance [53]. The polymer after-treatment reduces both relaxation and felting shrinkage almost independently of plasma treatment time.

There is more even and quicker penetration of dyestuffs and chemicals on plasma-

treated wool than the untreated reference sample. Fig. 14-12 shows the fibre cross-



Figure 14-12. Fibre cross-section of the untreated wool (enlargement 30 000X).



Figure 14-13. Fibre cross-section of the wool following plasma treatment (enlargement 30 000X).

section of an untreated wool fibre with the fibre stem (cortex) and the scale layer (cuticula), which is made up of the A- and B-layer of the cystine rich exocuticula and the cystine poorer endocuticula. Essentially A-layer of the exocuticula is changed by the plasma treatment. Fig. 14-13 reveals that the A-layer of the combed sliver is attacked to a different extent by the plasma treatment (glow-discharge) [54]. This manifests itself in a partially much reduced contrastability and gives the A-layer a “pearl-necklace like” appearance in the electron microscope. The increased dyes and chemicals affinity is presumably attributed to the plasma induced oxidation of the cystine in the A-layer of the exocuticula and thereby to a reduction of the wetting bridge density in the fibre surface.

Surface analyses of wool fibres treated with different plasma gases reveal that the wettability, wickability, printability and surface contact angle of the materials are significantly changed in a direction that may lead to new uses for these materials. Several aspects affect the web wettability, such as pore size, fibre diameter, fibre surface roughness and fibre surface chemical composition. Chemical composition of the fibre surface is most important as it determines the surface bonding forces with water, i.e. disruption force, polar force, and H-bonding force. Surface roughness is not a primary reason for improved wettability, but it may increase it [35].

Plasma treatment increases the hydrophilic groups in the wool fibre and the cystine present in the surface layer is converted to cysteic acid [55, 56]. The

endocuticle and the intercell membrane complex and the density of cross-links in the surface layer is decreased by the reactive species in the plasma gas and thus facilitate diffusion of dyes and chemicals [57]. The internal lipids of cell membrane complex are also modified to a certain extent [58]. These changes in the interior of the fibre are presumably caused by the short wave ultra-violet radiation which is produced by the low temperature glow-discharge plasma apart from the chemical active species such as electrons, radicals etc. [59,60].

Woollen sliver and yarn have been treated in low temperature plasma in a vacuum chamber for times from 20 to 30 min [61]. There is a significant increase in the strength which lead to better stability of the material during subsequent processing. Fabrics made from treated wool do not felt and also the shrinkage is reduced e.g. from 37% to 3-5%.

Plasma treated wool may exhibit more or less firm or harsh handle because of surface roughening. This property is very important for hand-knitting yarns or yarns for underwear fabrics. Softeners generally deteriorate the shrink resistance imparted by plasma treatment or plasma plus polymer after-treatment quite heavily [36]. The enzyme treatment is capable of improving the handle of plasma treated wool as well as plasma treated and polymer after-treated hand-knitting yarns without imparting their shrink resistance [62].

14.4.2 Plasma treatment of other fibres

Plasma may be used for removing the contaminants, finishing and sizing agents from the fabric. Desizing of polyester fabric that used polyvinyl alcohol as the sizing agent can be removed by plasma treatment [63].

The efficiency of scouring, mercerizing etc. depends on the penetration of water into the fibre and thus its wettability. The wettability of cotton and silk is increased a few fold due to its pre-treatment by N_2 plasma. In case of polyester fabrics also the wettability increases significantly.

The effectiveness of treating grey state and mercerized cotton and polyester/cotton blends in a low temperature plasma before dyeing is reported [64]. Both air and oxygen plasma treatment allowed the scouring process to be eliminated before dyeing.

A process has been developed for bleaching textile materials containing cellulose activated by microwave radiation [65]. High degree of whiteness and capil-

lary sorption are obtained. The bleaching can be carried out without silicate stabilisers with no increase in oxidation damage to the cellulose.

The hydrophobic effect on a woven cotton fabric can be obtained by surface treatment. Plasma treatment with acid as a component of original gas will result in a hydrophilic surface [66].

Polyester fibres can be effectively modified by low pressure plasma treatment. For yarns the plasma should be capable of being incorporated into the finished yarn production process, depending on the end-use of the yarn, alternatively it should be possible to add on a plasma treatment [67]. Treatment of polyester fibres by glow-discharge in air or oxygen causes a partial degradation of the fibre surface together with an increase in the capillary sorption of iodine or cations in aqueous solution [68]. Wetting out properties of polyester can be achieved by treatment of polyester with plasma and corona discharge [69]. The fabric can be processed without the use of a wetting out agent. Generally, polyester has a very hydrophobic surface because the surface is made up of ether oxygen (C-O-C) linkages while the hydrophilic ester oxygen (C = O) is facing towards the core of the fibre. When surface is treated by plasma either the ester oxygen (C = O) comes closer to the surface as a result of etching or some new C = O bonds are formed due to oxygen ions present in the plasma chamber.

Soiling of fabrics is another important aspect. Treatment of polyester with air plasma considerably decreases the soiling. During plasma treatment fabrics get negatively charged. The soils are also generally negatively charged and therefore there is increased repellency. The plasma etching increases the hydrophilic nature and therefore the soiling decreases. Etching by air plasma causes greater weight loss of nylon, cotton, silk or wool fibres than does etching by carbon tetrafluoride or nitrogen plasma. The degree of surface modification is lower for plasma etched nylon or polyester fibres than for cotton or wool fibres [70].

A small scale method for the preparation of linen fabric is described which practically eliminates the use of chemical reagents [71]. The grey fabric is treated in a glow-discharge plasma in air and then washed in hot water. The process maintains the strength of the fabric, does not affect the natural colour of linen and does give fabric a high degree of hydrophilicity [72].

The electron microscopic studies provide additional information regarding mor-

phological changes as a result of plasma treatment. Due to very low range of penetration the bulk structural property such as crystallinity of the sample is not much affected. Plasma etching alters the surface structure of cotton and silk considerably. The fibrillar structure is apparent only on the uppermost surface, whereas deep down it disappears. The surface of the polyester is very smooth initially, but plasma treatment produces a typical "sea-shore" structure. In addition in most of the fibres the plasma treatments give rise to the formation of some cracks, voids etc. The type of surface structure produced depends on the type of gas and pressure. For example, the use of nitrogen, oxygen, air and carbon dioxide for polyester gives distinct surface structure with striations and depressions. The use of CO_2 produces even more single crystal structures. On the other hand, the use of He, Ar, NH_3 gives low profile surface structures.

14.5 High Energy Radiation to Textiles

Energy sources fall conveniently into two groups, viz. high energy ionising radiation (X-rays, alpha particles, protons, deuterons, γ -rays and electrons) and low energy radiation (gas discharge and ultraviolet). In the case of radiation processing of textiles, only γ -rays from radioactive isotopes and high energy electrons (β -rays) from machines are needed to be considered. γ -rays are high energy electromagnetic waves and have great penetrating power. Among the radioactive materials recommended are Cobalt - 60 and Cesium - 137. 1-MeV gamma photons lose half their initial energy after passing through 10 cm of material of unit density. Only a small amount of available energy is in general utilised when textile materials are irradiated. The maximum dose rate from a powerful Cobalt - 60 source is about 2 M rad/h, and since several M rads are needed to effect significant changes in the material, long reaction times are generally needed. The irradiation source dictates the time of exposure. For example, radiation using ultraviolet lamp requires substantially longer times. However, the amount of radiation dosages depends on the kind of fibre (Table 14.1). It varies from 2 M rad for cellulosic fibres to that of about 40 M rad for polyester fibre (1 M rad = 10^8 erg/g of substance). With high energy radiation elaborate screening and safety measures are essential, capital costs are high, and the active material must be replaced from time to time. Nevertheless, γ -radiation is useful when low dose rates are required and when thick materials or rolls of fabric, are to be irradiated.

TABLE 14.1

Guide Values of Irradiation Dosages [73].

Substrate	Radiation dosage M rad
Cellulose	2-3
Cellulose/synthetic	2-3
Polyamide	5
Polyacrylic	5
Polyester	40

Certain fibre forming polymers have been reported to degrade and to cross-link on exposure to high energy radiation. The relative extent of degradation and cross-linking varies from fibre to fibre and is dependent upon radiation dose, temperature, and whether air is excluded during irradiation [74-77]. Degradation predominates in cellulosic fibres, cellulose acetates, wool, poly (vinylidene chloride) and polytetrafluoroethylene, whereas polyethylene, polypropylene, polyamides, polyesters and polyacrylonitrile are more susceptible to cross-linking [78].

The result of the introduction of radiation with a polymer is the creation of free radicals. These frequently result from the breaking of C-H bonds leaving a polymer radical. The latter usually abstracts another hydrogen forming hydrogen gas and another polymer radical. The fate of the radicals determines whether the polymer chain degrades or forms cross-links. The mechanism by which these cause effective cross-linking is not clear but presumably the monomer adds to the macromolecule before cleavage, just as in the grafting process [79].

The use of high energy radiation for the bleaching of textile materials has been patented [80]. A wide range of possibilities exists for modifying both the physical and the chemical properties of textiles. Bleaching of textiles can be done either by radiating the bleach bath before the entry of the fabric into the bleaching solution or the fabric may be exposed to radiation and stored and then bleaching is carried out. The bleach bath containing sodium chlorite (5 - 110 g/l) can be activated by high energy radiation, with pH adjusted to 9 to 11. The application baths also contain other usual additives such as optical brighteners, wetting agents and auxiliaries and bleaching can be done using continuous or batch methods at or below normal pro-

cessing temperature. The free radicals are formed when textile materials are subjected to moderate amounts of radiation (1-2 Mrad), so that the fibre degradation can be kept to minimum.

The potential of ultra-violet or electron beam curing treatments on textiles needs further investigation as such treatments have been used in surface coating treatments in the packaging industry [81]. The use of appropriate polymer systems with appropriate functional performance properties for use with such treatments may be particularly valuable for surface treatments using UV curing, although electron beam curing is an expensive technique [82-84].

Gas phase or vapour phase treatments is not yet popular in wet processing of textiles. However, in the area of garment finishing, the difficulties of treatment by any other method potentially render gas phase treatments attractive, particularly for treatment of a composite multiple layers of fabrics, such as in a garment [85, 86].

REFERENCES

- 1 K. R. Makinson and J. A. Lead, Proc. 5th Int. Wool Text. Res. Conf., Aachen, Vol. 3 (1975) 315.
- 2 A. E. Pavlath and K. S. Lee, Proc. 5th Int. Wool Text. Res. Conf., Aachen, Vol. 5 (1975) 263.
- 3 M. M. Millard, Proc. 5th Int. Wool Text. Res. Conf., Aachen, Vol. 2 (1975) 44.
- 4 K. S. Lee and A. E. Pavlath, Textile Res. J., 45 (1975) 625, 742.
- 5 K. S. Lee and A. E. Pavlath, Textile Res. J., 50 (1980) 42.
- 6 A. E. Pavlath and K. S. Lee, Makromol Sci. Chem., A 10 (3) (1976) 619.
- 7 N. N. Beilajev, Tiekst. prom., 5 (1977) 37.
- 8 W. Rakowski et al., Melliand Textilber., 63 (1982) 307.
- 9 W. Rakowski, Melliand Textilber., 70 (1989) 780.
- 10 H. L. Röder, J. Textile Inst., 44 (6) (1953) 247.
- 11 French P 1, 197, 146 (1959).
- 12 German Patent DE 4349 427 A 1 (Sando Iron Works, Japan).
- 13 Ciba-Geigy, European P 0559609.

- 14 Ciba-Geigy, European P 0548013.
- 15 J. Hirai and O. Nakada, *Jpn. J. Appl. Phys.*, 7 (1968) 112.
- 16 H. Yasuda, *J. Polym. Sci., Macromol Rev.*, 16 (1981) 199.
- 17 H. Yasuda and T. Hirotsu, *J. Polym. Sci., Polym. Chem. Ed.*, 16 (1978) 228.
- 18 J. Goodman, *J. Polym. Sci.*, 44 (1960) 551.
- 19 P. Kassenbeck, *Melliand Textilber.*, 39 (1958) 55.
- 20 A. E. Pavlath and R. F. Slater, *Appl. Polym. Symp.*, 18 (1971) 1317.
- 21 B. S. Split, *Polymer*, 4 (1963) 109.
- 22 H. Z. Jung, T. L. Ward, R. R. Benerito, *Textile Res. J.*, 47 (1977) 217.
- 23 C. I. Simiontscu, F. Denes, M. M. Macoveanu and I. Negulescu, *Makromol Chem. Supplem.*, 8 (1984) 17.
- 24 W. J. Thorsen, *Appl. Polym. Symposium*, 18 (1971) 1171.
- 25 G. A. Byrne and D. M. Jones, *J. Soc. Dyers Colourists* (Dec 1971) 496.
- 26 S. Kanazawa, M. Kogoma, T. Moriwaki and S. Okazaki, *J. Physics D.*, 21 (1988) 838.
- 27 N. Kanda, M. Kogoma, H. Jinno, H. Uchiyama and S. Okazaki, *Proc. 10th Int. Symp. on Plasma Chemistry, Vol. 3* (1991) 201.
- 28 J. R. Roth, *Industrial Plasma Engineering : Vol. I – Principles*, Ch. 12, Institute of Physics Publisher, Bristol, U. K., 1995.
- 29 J. R. Roth, P. P. Tsai and C. Liu, U. S. patent 5,387,842, Feb. 7, 1995.
- 30 J. R. Roth, P. P. Tsai, L. C. Wadsworth, C. Liu and P. D. Spence, U. S. patent 5,403,453, Apr. 4, 1995.
- 31 J. R. Roth, P. P. Tsai, C. Liu, M. Laroussi and P. D. Spence, U. S. patent 5,414,304, May 9, 1995.
- 32 J. R. Roth, P. D. Spence and C. Liu, *APS Bull.*, 38 (10) (1993).
- 33 J. R. Roth, *Industrial Plasma Engineering : Volume II – Applications*, Institute of Physics Publisher, Bristol, U. K., 1997.
- 34 J. R. Roth, L. C. Wadsworth, P. D. Spence, P. P. Tsai and C. Liu, *Book of Papers, TANDEC 3rd Annual Conference*, Knoxville, TN, Nov 1-3, 1994.
- 35 P. Tsai, L. C. Wadsworth and J. R. Roth, *Textile Res. J.*, 67 (5) (1997) 359.
- 36 W. Rakowski, *J. Soc. Dyers Colourists*, 113 (1997) 250.
- 37 A. Bradley and J. D. Fales, *Chem. Tech.*, (1971) 232.
- 38 F. H. Fredich, *Acta Chemica Hungaria*, 125 (1985) 165.

- 39 G. Franz, *Kalte Plasmen*, Springer, Verlag, Berlin, 1990.
- 40 G. A. Carnaby, *Proc. 9th Int. Wool Text. Res. Conf. Biella*, Vol 4 (1995) 430.
- 41 German waste water legislation, Bonn (5 Mar 1987) (amendment of 1986 legislation).
- 42 A. E. Pavlath, *Techniques and Applications of Plasma Chemistry*, Eds. J. R. Hollahan, A. T. Bell, John Wiley & Sons, New York, 1974, pp 149.
- 43 A. E. Pavlath, *J. Polym. Sci. Polym. Chem. Ed.* 12 (1974) 2087.
- 44 J. Ryn, T. Wakida, H. Kawamura, T. Goto and T. Takagishi, *Chem. Express*, 2 (1987) 377.
- 45 W. Rakowski, *Plasma Treatment of Wool*, 1992, Biella Wool Textile Award, Citta degli Studi Biella (Publ.), Italien.
- 46 M. Lee, J. Ryn, T. Wakida and Y. Sato, *Chem. Express*, 7 (1992) 241.
- 47 H. L. Roder, *J. Textile Inst.*, 44 (6) (1953) 247.
- 48 E. H. Mercer and K. R. Makinson, *J. Textile Inst.*, 37 (1946) 269.
- 49 J. Lindberg, *Textile Res. J.*, 18 (1948) 480.
- 50 W. Rakowski, *Proc. 9th Int. Wool Text. Res. Conf., Biella*, Vol. 4 (1995) 359.
- 51 M. Bona, E. Pirna and F. Ramazio, *Proc. 9th Int. Wool Text. Res. Conf., Biella*, Vol. 5 (1995) 230.
- 52 L. L. Gorbeg et al., *Tekstilprom.*, 11 (Nov 1989) 43.
- 53 K. M. Byrne, W. Rakowski, A. Ryder and S. B. Havis, *Proc. 9th Int. Wool Text. Res. Conf., Biella*, Vol. 1a (1995) 234.
- 54 H. Thomas, J. Herring, W. Rakowski and H. Hocker, *Int. Textile Bull.*, 2 (1993) 42.
- 55 M. M. Millard, *Proc. 5th Int. Wool Text. Res. Conf., Aachen*, 11 (1975) 44.
- 56 T. Klausen, *Diplom-Arbeit RWTH, Aachen*, 1992.
- 57 M. Lee and T. Wakida, *Sen'i Gakkaishi*, 48 (1992) 699.
- 58 F. S. Lee, *Textile Res. J.*, 46 (1976) 779.
- 59 H. Yasuda, *J. Macromol. Sci. – Chem.*, A 10 (1976) 383.
- 60 D. T. Clark and A. Dilks, *J. Polym. Sci., Polym. Chem. Ed.* 18 (1980) 1233.
- 61 V. K. Afans'ev, T. M. Aleksandrova and M. N. Serebrenikova, *Tekstilprom.*, 8/9 (1993) 34.
- 62 S. M. Smith et al., *Proc. 9th Int. Wool Text. Res. Conf., Biella*, Vol. 3 (1995) 335.

- 63 R. Riccobono, *Textile Chem. Color.*, 5 (1973) 219.
- 64 A. L. Tsriskina, J. N. Gushchina, B. L. Gorberg and A. A. Ivanov, *Referat. Zhur.*, 42 B (July 1991) 7.
- 65 E. L. Grigoryan and S. M. Gubina, *Referat. Zhur.*, 12 B (Nov 1990) 11.
- 66 M. Rabe, *Diplomarbeit, Fachhochschule Niederrhein, Mönchengladbach*, 1991.
- 67 M. Rabe et al., *Melliand Textilber.*, 75 (1994) 506.
- 68 M. V. Yasuda, I. B. Blinicheva and A. I. Maksimov, *Vyssh. Ucheben. Zaved. Khim. Khim. Tekh.*, 24 (1981) 1143.
- 69 S. Ruppert, B. Müller, T. Bahners and E. Schollmeyer, *Textil Praxis*, 49 (1994) 614.
- 70 T. Yasuda et al., *Mukogawa Joshi Diagaku Kiyo Shokumolsu-Ken.*, 30 (1982) A9.
- 71 E. L. Vladimirtseva, L. V. Sharina and B. Blinicheva, *Referat. Zhur.*, 12 B (Aug 1994) 8.
- 72 N. M. Krach, T. V. Tyurkina, S. F. Sadova, E. V. Naumov and A. S. Kechikyan, *Textilprom.*, 1/2 (1995) 32.
- 73 E. S. Olson, *Book of Papers, AATCC Int. Tech. Conf., Montreal, Canada* (1976) 156.
- 74 F. R. Leavitt, *J. Polym. Sci.*, 45 (1960) 536.
- 75 F. R. Leavitt, *J. Polym. Sci.*, 51 (1961) 341.
- 76 G. A. Byrne and D. M. Jones, *J. Soc. Dyers Colourists*, (Dec 1971) 496.
- 77 V. Stannett, *Amer. Dyestuff Rep.*, (May 1965) 374.
- 78 V. Stannet and A. S. Hoffman, *Amer. Dyestuff Rep.*, 57 (1968) 998.
- 79 S. R. Karmakar and P. P. Kulkarni, *Synthetic Fibres*, 23 (4) (1994) 7.
- 80 Hoechst, AG, *British Patent* 1, 397, 595 (11 June 1975).
- 81 I. Holme, *Colourage, Annual* (1998) 41.
- 82 I. Holme, *J. Soc. Dyers Colourists*, 110 (12) (1994) 362.
- 83 Albright & Wilson, *Technical Information Leaflet, ITMA 95, Milan, Italy*.
- 84 G. H. J. Van der Walt, and Van Rensberg, *N. J. J. Text. Prog.*, 2 (1986) 14.
- 85 M. M. Morris, C. E. Morris and E. A. Catalano, *AATCC Int. Conf.*, (1996).
- 86 M. M. Morris, C. E. Morris and E. A. Catalano *Textile Chem. Color.*, 28 (8) (1996) 50.