Safety Precautions and Efficient Handling of Hazardous, Toxic and Volatile Chemicals in the Pulp and Paper Mills

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ABSTRACT

The Indian Paper Industry has registered a 50% growth during the sixth plan period from a level of 13 lac tonnes installed capacity in 1979-80 to more than 24 lac. tonnes by 1984-85. This rise in production capacity also demands large quantities of raw materials and chemicals usage in the industry

Newer technologies based on increasing use of chemicals which are either Toxic or Hazardous in handling/usage, are also making inroads in the Industry.

It is important that their correct usage, information data on properties etc and chemistry is made available to the operating personnel.

Most chemicals and propriatory products used in the Paper Industry today, have been classified in the following four categories

a) General, non hazardous non toxic chemicals
Rosin, Alum, Soap-stone powder, China clay, Starches, Gums, Titanium Dioxide, Ultra marine Blue, Optical Brightners, Dyes etc.

b) Hazardous chemicals
Sulphuric acid, Caustic soda, Chlorine (gaseous), Calcium-Sodium Hypochlorit, Acetic acid, Lime, Sodium Sulphide etc

c) Newer Organic High polymeric based chemicals and propritary products which are either Toxic or Hazardous.

Synthetic Rubber Laticis Acrylic monomers and High Polymeric formulations, Urea formaldehyde/Malamine formaldehyde based wet strength compounds, Retention aids, Slimicides and Pesticides, etc.

d) Poisonous/Toxic chemicals used in laboratories
Potasium cyanide, Terricyanide, Sulphocyanides. Volatile organic solvents, Sodium nitrite, Iodine, Bromine etc.

The chemicals have have been classified according to their use in the different stages of Pulp and Paper making. These include chemicals, bleaching chemicals, wet and additives, coating and surface application chemicals, slimicides/fungicides and chemicals used in other diverse applications.

The various physico chemical properties of these products have been discussed with more emphasis on hazardous chemicals and the handling and safety precautions that needs to be taken in their use.

An attempt has also been made to forward a general scenario remedial strategies in case of accidents arising in handling of such chemicals.

It has been particularly emphasized that though most of these chemicals are very common and need only simple handling and safety precautions to be followed, they are ultimately handled by workmen who posses very scant knowledge about their correct handling and safety measures. Hence it is of prime importances that operators should be properly educated in all the safety aspects in handling these chemicals.

Lastly chemicals used in Research & Development Laboratories have also been covered with some useful recommendations in their handling.

Contrary to the ancient art of paper making, today a great deal of sophistication has come in the modern technology of paper making.

The stress is on automatic controls and continuous processing machines using computerized systems and the latest concepts of Chemical Engineering.

Equally important is the Chemical Technology aspect which requires the careful and judicious use of Modern chemicals and product formulations for manufacture of speciality and quality papers.

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It is therefore essential to know such products and their physical as well as chemical properties, so that their use become safe and economical.

The Indian Paper Industry registered a 50% growth during the sixth plan period from a level of 13 lac tonne installed capacity in 1970 - 80 to more than 24 lac tonne by 1984 - 85. This rise in production capacity also d.mands proper usage of large quantities of raw materials and chemicals in the industry.

Newer technologies based on increasing use of chemicals which are either toxic or hazardous in handling are making inroads in the industry. It is of prime importance that their correct handling, information data on properties etc and chemistry is made available to the technologists.

2 The various chemicals used in Pulp and Paper Industry can be clasified according to their end use in different departments.

2.1 Pulping Chemicals :

There are two distinct chemical pulping process, viz, Sulphite and Sulphate process. The former utilises acidic medium (mainly) and the latter basic medium to delignify the wood. The basic chemicals are listed in Table No. 1.

TABLE No. 1

Sl. No.	Particulars of department	Chemicals used
1	**Pulping chemicals :**	
	a) Sulphite process	Calcium/Magnessium/Ammonium Sulphites, Bisulphites, Sod. carbonates, Sod. Hydroxide etc
	b) Sulphate process	Sod. Hydroxide, Sod. Sulphide, Sod. Sulphate, Sod. Carbonates, Anthraquinone etc.
2	**Bleaching chemicals :**	Chlorine, Chlorine dioxide, Ozone, Sod. Hydroxide, Sod./Calcium hypochlorite, Sulphamic acid, Sulphuric acid, Oxygen peroxides, Hydrosulphites etc.
3	**Wet end additives :**	
	a) Sizing chemicals	Alum, Rosin, Silicates, Waxes, Octa decynyl-succinic anhydride (OSA) Alkyl ketene diamer (AKD) and other propritory products etc.
	b) Wet strength additives	Urea/Malemine formaldehyde, starches, gums, proteins latexes, Polymeric condensed products, etc.
	c) Retention and drainage aids	These includes high molecular compounds containing specific charged ions, flocculents etc.
	d) Optical brightness	Benzene derivatives, Ultramarine blue
	e) Dyes	Rhodamine, Methyl blue, Auromine, congored etc.
	f) Loading chemicals	Talc, clay, titanium dioxide, silica and its compounds, calcium carbonates etc.
4	**Coating and converting chem'cals :**	
	a) Pigments	Clay, titanium dioxide calcium carbonates, Talc, satin white, amorphus silica, zinc oxide pigments Barium sulphate etc.
	b) Binders	Starches, casein soya protein CMC, styrene - butadiene latexes, Acrylic emulsions PVC, PVA etc.
	c) Additives	Polyphosphates, alkali silicates anionic polymer dispesants etc.

Recently enough, Anthroquinone and many of its derivatives are also being used as pulping aids.

2 2 Bleaching Chemicals :

Mainly oxidative or reductive chemicals are used. This particular section utilises the most hazardous/ poisonous Chlorine and its dioxide in bleaching process. These chemicals are also listed in Table No. 1.

2.3 Wet end additives :

These are the chemicals used in wet end section of paper making to develop certain properties in the finished paper. Depending upon their specific use they are further subdivided into different catagories. They are viz.

a) Sizing chemicals.
b) Additives for wet and drv strength improvement.
c) Retention and drainage aids.
d) Optical brightners.
e) Dyes.
f) Loading chemicals.

Table No. 1 gives a detail tabulation of these chemicals.

2.4 Coating and converting chemicals :

There are series of different chemicals under this group. They can be further divided as :

1) Pigments.
2) Binder or adhesive and
3) Additives.

Table No. 1 gives an account of the chemicals.

2.5 Chemical Recovery Section :

Chemicals handled in this section are very hazardous not only because of their chemical nature but of their physical conditions (such as high temperature and concentration etc.

They are viz,

Caustic lye, white liquor, black liquor, green liquor, Lime, Sodium Sulphate, Sodium carbonate (molten) etc.

3.0 All these chemicals and proprietory products have been further subsivided into the following four groups.

3. a) General, non hazardous, non toxic chemicals :

This group includes chemicals like Rosin, Alum, Soap stone powder, China clay, Starches, Gums, Titanium dioxide, Ultramarine Blue, optical brightness, etc.

The above listed chemicals do not pose any handling/safety problems either in solid state or in liquid form. As these chemicals are non poisonous in nature, contact with human body does not pose any health hazards. Generally speaking, any spillage on ground or body should be washed with abundent quantity of water.

Recently, powder form of Rosin is also being used by the industries, such as fortified rosin and of its type. This powder is combustible if it comes in direct contact with fire. Proper care should be taken to avoid any fire hazard.

However, some general recommendations for storage and safe handling are as follows :

a) Some chemicals listed, are combustible and also deteriorate in quality if stored in direct sunlight or kept open exposed to moisture, humidity etc.

b) Alum reacts slowly with atmospheric humidity and produces Sulphuric Acid. Thus it should be stored in a dry place and also protected from heat.

c) Optical brightening agents are very sensitive to direct light and sunlight. They should be stored in air tight containers and should not be exposed to sunlight.

3. b Hazardous chamicals :

This group includes the following chemicals — Sulphuric acid, Caustic lye, Chlorine (Gaseous) Calcium/Sodium Hypochlorite, Lime etc.

General properties and hazardous effects are listed in the Table No. 2.

TABLE No. 2

Sl. No.	Chemicals	Specific gravity	Boiling point	Permissible Maxima for atmospheric contamination in PPM	Aquatic toxicity
1	Chlorine	1.424	– 31.4°C	5	0.08 ppm/168 hr/trout/TLM/Fresh water 10 ppm/1 hr/tunicates/killed/Salt water
2	Sulphuric acid	1.84 at 20°C	34.0°C	10	24.5 ppm/24 hr/bluegill/lethal/F.W. 42.5 ppm/48 hr/Prawn/LC_{90}/Salt water
3	Caustic lye	2.13 at 20°C (solid)	very high	—	125 ppm/96 hr/mosquito/TLM F.W. fish 180 ppm/23 hr/oysters/lethal/Salt water

Chlorine being the most hazardous chemical some basic precautions are always needed to avoid any accidents in its handling.

Storage of chlorine cylinders should be done in open shed and two cylinders should be placed with sufficient space in between them. Proper ventillation is a must if the cylinders are stored in closed godowns.

As chlorine gas is highly corrosive, stainless steel/ PVC pipe lines are recommended for its transportation and use in process equipments. Operating personnel should be provided with gas masks to avoid respiratory track exposure with chlorine. Workmen should also be provided with goggles and rubber overclothing as a safety precaution.

Chlorine is a greenish yellow gas with irritating bleach like choking smell. It is not combustible but poisonous gases are produced in case of external fire.

If the vaporus are inhaled-the victim should be immedlately brought to fresh air and artificial respiration should be started. But mouth to mouth respiration is not recommended in such cases. In case of heavy inhalation of chlorine vapours, Oxygen respiration should be continued till proper medical aid is available, Chlorine, when inhaled quickly reacts with the aqueous fluids in the respiratory track producing Hydrochloric acid. This not only produces dehydration of the soft and delicate tissues, but causes acid burns.

The operating valves of chlorine cylinders should be frequently chacked for leakages and malfunctioning, Chlorine leak is immediately detected due to the strong and pungent smell of chlorine gas. The main supply should be immediately stopped in case of leakage, and all windows, doors should be opened for ventilation. All sections where chlorine is used must be provided with exhaust fans. However, since chlorine is heavier than air it tends to settle down. Hence ventilation fans placed at ground levels are most effective.

Some times a spray of Ammonia also quickly neutralizes the chlorine gas, through forma ion of a white misty vapours of Ammonium chloride which quickly settles down.

Fatal accidents occur sometimes due to mishandling of leakaging chlorine cylinders. These cylinders should never be dumped in nearby rivers or water tanks/reservoirs where fish and other aquatic life exsists. These species die in large numbers and their bodies decay in the water, causing health hazards to the entire population which use this water for drinking purpose.

The next dangerous chemical is concentrated sulphuric acid. Storage of acid should be preferably done in cylinderical tanks which have been properly listed for specified hydraulic pressures. Inner surface of storage tank should be coated with either PVC/epoxy coatings or lead lined.

For transportation of acid within the premise, all pumps, impeller, pipe lines, valves should be made of Stainless steel to avoid corrosoin and subsequent leakage of acid. Safety goggles and handgloves are very essential for persons who are handling sulphuric acid.

Sulphuric Acid should be always diluted by adding the concentrated acid to a large volume of **Cold** water while constantly stirring to dissipate the heat generated. If water is directly added to concentrated H_2SO_4 the entire mixture will explode.

In case of accidents/burns due to spilling of acid the affected area should be washed with plenty of water. If the vapours are inhaled the victim should be brought to fresh air, artificial respiration should be given. Water or preferably milk should be made available to the victim. There should not be any induced vomiting to such victims

Handling of caustic lye has also to be done very carefully. Usual safety equipments has to be provided to the workers. One should always check that the stored caustic lye is not open to the atmosphere. In such cases, caustic lye will absorb atmospheric carbon dioxide to form carbonates which will subsequently lower the strength of solution.

Any spillage should be washed with abundent quantity of water. Storng solution of caustic soda cause severe burns to the skin and hands if direct contact is made. Hence solutions of caustic soda should be always handled with rubber gloves and gum boots.

Extra care should be taken while preparing fresh caustic soda solutions with flakes or solid NaOH. Considerable heat is generated when NaOH is added to water. Hence the preparation should be carried out carefully and slowly.

Hypochlorite and lime are less hazardous in comparison with other chemicals cited abovc. Hypochlorite being a weak alkali does not always pose any serious problem to the extent of being dangerous.

Lime which is handled in very fine powder form needs, some special attention, Air filter masks are very necessary for the persons handling lime.

Sodium Hypochlorite NaOCl is often prepared by a slow bubbling of Cl_2 gas in caustic soda solution. In such a casc precautions mentioned earlier for NaOH and Cl_2 should be carefully followed.

3. c) Newer organic High Polymeric Chemicals and Propriatory Products which are either toxic or hazardous

This group includes chemicals like Synthetic rubber laticies, Acrylic monomers and high polymeric formulations, Urea formaldehyde/malemine formaladehyde wet strength compounds, Retention aids, Slimicides and pesticides etc.

Laticies and high polymeric formulations are newer chemicals now widely used in the industry for coating/ high gloss finishes and as retention aids/floculating aids.

It is normally recommended that such chemicals should be stored in such a way that they are not exposed to extreme of temperatures. Recommended storage temperature is + 10°C to ± 40°C. During the period of extended storage these chemicals show a tendency towards creaming and pH variations. Such tendencies are more prevalent when the chemicals are stored at high temperature. Periodic agitation in the containers normally prevents creamings. In some cases it is advisable to filter the chemicals before use, since foam formation and consequent drying of particles as well as skin formation on container walls or closure may occur during transportation or storage.

As these chemicals having water as main component, are considered non flamable. To the extent possible direct physical contact with such chemicals shou d be avoided. It is recommended that suitable eye protection and hand-gloves should be used while handling. Any spillage should be washed away wiih sufficient quantity of water.

Chemicals for wet strength papers

Some special precautions for Urea Formalhyde/ Melamine formaldehyde based wet strength chemicals are as follows :

These chemicals are prepared by reacting Urea and Melamine $C_3H_3(NH_2)_3$ with Formaldehyde HCHO either at room temperature or by Refluxing. The final product is a condensate, which normally contains 5-7% of free or excess formaldehyde.

Formaldehyde by itself is a gas which is soluble in water and is usually sold as Formalin which is a 37% aqueous solution. It has a strong pungent odour and is extremely irritating to the skin and eyes. Hence proper care should be taken while opening closed containers of Wet strength chemicals, Formaldehyde vapours should not be inhalded directly while handling the chemicals.

Retention and floculating aids

Some of the popular retention and floculating aids are mixtures of polyacrilamides, Polyacrylic Acid and derivators of Methyl Metacrylates,

$(CH_2 - CH)_n$ | $CO\,NH_2$ — Polyacrylamide

$(CH_2 - CH)_n$ | $COOH$ — Polyacrylic acid

$(CH_2 - C\,CH_3)_n$ | $CO\,OCH_3$ — Polymethyl Methacrylate

These formulations also contain a small percentage of the free monomers which should be handled very carefully.

These vinyl monomers and polymers are sometimes highly toxic and irritant to the skin.

Propriatory formulations which contain either Acrylic Polymers or their free monomers should be handled with extreme care.

Frequent contact with skin may cause dermatitis skin allergy and their inhalation may cause giddiness, fatigue and other adverse symptoms.

In no case such compounds may be handled with bare hands. Containers should be kept safely and properly labelled.

3. d) Poisonous/Toxic chemicals used in laboratories

This group contains chemicals like Potasium cyanide, Ferricyanide, Sulphocynides, Volatile organic solvents, Sodium nitrite Iodine, Bromine etc.

There are several chemicals used in R & D laboratories which vary from highly poisonous to stable neutral chemicals.

Handling of volatile chemicals is always a risky job. For example while opening a bottle of liquor ammonia the contents should be cooled down to room temperature or even below; otherwise the contents of the bottle may spray on ones body. Many organic solvents are highly combustible. Even slight amount of contamination will result in violent explosion. For example if Diethy either contains a very small amount of Hydrogen peroxide as a contaminent; the mixture will explode during its evaporation. And so the person handling such chemicals should always test for its contaminants and those are to be properly neutralised before use.

All the compounds of cynides are highly poisonous, Pipetting of such chemicals should be done with great care using automatic syphones and drop pippettes. Such chemicals, as well as strong acids, alkalis and other harmful reagents should not be sucked in the pipette by mouth. Slight contact with body will prove fatal.

Storage instructions are always supplied with the chemicals. These are to be forcefully followed. Direct sunlight should be totally avoided in storage for example if chloroform is exposed to sunlight for few hours it will be oxidised to form a highly poisonous gas called phosgene which is again soluble in chloroform itself Such adulterated chemicals when used will prove fatal.

4. Labour relations in safety

It is of prime importance that though most of the chemicals used in paper industry are very common and need only simple handling and safety precautions, they are ultimately handled by workers who possess very scant knowledge about their correct handling and safety measures.

Safety hazards are potential deterrents to attainment of optimum technical efficiencies and product quality. It is necessary to properly educate and train the group foremen in the correct procedures for handling these chemicals.

Very often, correct information regarding the hazards and toxicity of chemicals or products is withheld from those who actually handle such chemicals at the shop floor, for fear of resistance or demands for a compensation.

This is not very prudent on the part of technologists/managements, since very often through such a practice, they escape with provisions for even basic safety appliances e.g. gloves, goggles and rubber boots etc.

Proper care, supervision and frequent training programmes and group discussions will help a long way in avoiding undue wastage, accident hazards and health hazards.

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