Pulp and Paper Workers, and Paper Dermatitis

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1 Core Messages

- Pulp and paper manufacturing are complex industrial processes. Pulp mill operations are becoming more automated. Operating personnel spend more time in the control rooms, away from the industrial process. This fact minimizes the workers' exposure to hazardous substances.
- The most common chemical pulping process is the sulfate (kraft) method followed by bleaching of pulp. Sulfite pulping is suitable for producing cellulose from spruce wood. "Sentence should be next to the bullet point!"
- Chlorine dioxide, sulfur dioxide, hydrogen sulfide, nitrogen dioxide, and ozone are hazardous gases which may cause mucous membrane irritation and intoxication.
- Pulp and paper workers are at risk of developing respiratory and gastrointestinal cancer and hematologic malignancies due to exposure to multiple cancerogenic substances at their workplaces.
- Contact dermatitis is rare among pulp and paper workers. Only 1.3% of the workers in a Swedish wood-pulp factory had work-related dermatitis. This prevalence corresponded to the frequency in the mean population. In a Dutch paper mill, however, irritant contact dermatitis was seen in 26% of the workers; 36% of them were diagnosed with mycosis of the feet.
- Slimicides and their constituents – potent biocides – are the most prominent agents causing allergic contact dermatitis among pulp and paper workers.
- Colophony (Rosin) and formaldehyde are the most important allergens causing paper dermatitis.
- Carbonless paper (NCR paper) is no hazard to the health of either paper workers or users, and has only a small potential for producing mild and transient skin irritation.
- Duplicating paper, in general, is a safe process, since there are only few case reports about allergic contact dermatitis due to the chemicals involved. Ammonia as an irritant gas may be released by the diazo process.
- Biocides used as preservatives in wet toilet paper are potent contact allergens. In contrast, perfume in hygiene paper is a negligible source for sensitization.

2 Introduction

Paper is defined as a felted sheet made of natural fibers – primarily derived from wood – which are compressed several times. It has always been used as writing or packaging material.

The word "paper" is derived from the Greek word for the Egyptian writing material papyrus, which was invented more than 5000 years ago and used by the Egyptians, Greeks, Babylonians, and Romans. Cai Lun, an official within the Chinese Han Dynasty, is widely accepted as the person who invented the modern paper making process in AD 105(Wikipedia 2010). This original paper was made of diverse plant fibers and worn cloths. Cai Lun's crafting process, using hard plant fibers, a heavy wooden stamp, and a stone mortar, is still the basic principle used in modern paper manufacturing.

During the Arabian-Chinese War in the eighth century, some Chinese prisoners who were paper workers were brought to Samarkand (Uzbekistan). They taught the Arabs the art of papermaking. During the expansion of the Arabian and Moorish empire in North Africa and Spain, paper found its way to southern Europe. Paper production in Europe began in southern Spain in AD 1144. The first European paper mill was built in 1276 in Ancona (Italy). The paper manufacturing sites were called "paper mills" due to the process of using a water-powered mill wheel to stamp fibers on a strainer. The papermaking process spread throughout Europe, and saw many innovations (Neathery de Safita 2002). In 1670, a revolutionary cylinder machine, called "The Beater," which replaced the original stamping process was invented in the Netherlands (Freyer 1999). The first integrated paper machine, which was also the first assembly line in history, was built by Louis Nicolas Robert in 1799 in France. For the first time, it was possible to mass-produce paper on a continuously running machine powered by a crank handle. Until then, all paper produced had been made by hand. Charles Fenerty (Canada) and Friedrich Gottlob Keller (Germany) independently experimented with wood pulping and published their results in 1844; they developed modern wood-based paper manufacturing. Since then, several improvements concerning the use of raw materials and the procedures have been made, primarily in France, Great Britain, Germany, and in the United States (Burger 2007).

Today, modern paper machines produce more paper in 1 h than nineteenth century machines produced in 1 year. The basic process, however, has not changed in the last 500 years. The sheet is still created on a strainer, compressed mechanically, and dried with heat. Modern paper machines are equipped with a checking device to measure the quality of the sheet during the production process. The final quality control, nevertheless, is still made by the skilled paper worker. In Germany, an apprentice undergoes a 3-year training in a technical college to become a fully skilled paper worker. He can become an engineer of paper manufacturing after further education.

With the inexorable advance of new electronic communication technologies, a paperless world was predicted by many people, but was never realized. Three hundred and eighty-one million tons of paper were produced in 2006. By 2020, the global production in the pulp, paper, and publishing sector is expected to increase 77% above the level of production in 1995. Forty-two percent of the global wood harvest for industrial uses goes to paper production (Abramovitz and Mattoon 1999). The paper industry is divided into four subgroups, representing the different types of paper:

Graphic and writing paper
Paper and cardboard for packaging
Hygiene paper
Paper and cardboard for technical use

The leading paper production countries are the USA, Canada, China, Japan, and Germany. While the per capita consumption of paper is 58 kg worldwide, the USA's per capita consumption is 301 kg. The average EU citizen consumes 186 kg of paper every year (Verband Deutscher Papierverbricken 2008).

In a world influenced by an increasing ecological awareness and a general shortage of resources, paper is an excellent material. Compared to other materials, such as plastic, the majority of all papers can be recycled several times. In practice, paper fibers can be recycled up to six times before they cannot be used anymore. But even in the recovery process, a certain amount of fresh fibers must be added. The paper industry also contributes to the preservation of sound forests, as the major part of the wood which is actually used for the paper production consists of waste wood and thinning material. This timber must be cut anyway to maintain the quality of the forest.

3 Thermo-Mechanical Pulping (TMP)

Pulp and paper production are complex industrial processes. Chemicals may be used during any of the multiple stages of the process. Bonds in the wood are broken down by pulping either by mechanical means or by chemical means. In order to produce pulp free of dark spots and dirt, the trunks and logs are debarked, usually in drum barkers. The bark is removed from the logs by friction caused by the rotating drum. Hot water may be added, but no chemicals are used in debarking. After debarking, the pulpwood is chipped to fragments about 10–30 mm long and 2–5 mm thick. No chemicals are used in the chipping process. A variant of this refiner process is the "thermo-mechanical pulp" method (TMP method) in which the fibers of the wood chips are broken under vapor pressure at 130 °C (Ahrens and Jöckel 1996).

4 Sulfate (Kraft) Pulping

In Germany, the sulfate (kraft) method was established by Dresel and Dahl in 1879. Thus, for the first time, lignin could be removed by chemical means. It is used in about 80% of current industrial pulping processes, especially in Scandinavia and North America. Other processes involve the sulfite method, ground wood, and semi-chemical technique (McGill 1980; Purssell 2010).

Stored outdoors, the chips undergo wood loss due to degradation, mainly caused by fungi. Biological processes lead to a rise in temperature inside the chip pile. The chip-pile workers are exposed to fungal spores and volatile chemicals derived from the wood, e.g., terpenes, formic acid, aldehydes, and ketones. The chips are fed into the pulping process by a screw-reclaiming system and conveyor belts. They are broken down by heating them at 170–180 °C for 1–3 h in *white liquor*, a mixture of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). Sulfate pulping was named after sodium sulfate (Na_2SO_4) which is added to *black liquor* during cooking, and is reduced to sodium sulfide (Na_2S) by combustion. It is an alkaline process at pH 14. NaOH causes swelling of the wood chips and supports the penetration of the alkaline solution. During this initial pulping process, the following chemical equilibrium is crucial:

$$NaOH \rightarrow Na^+ + OH^-$$

$$Na_2S + H_2O \rightarrow HS^- + 2\,Na^+ + OH^-$$

$$HS^- + H_2O \rightarrow H_2S + OH^-$$

On the one hand, methoxy ligands (CH_3O^-) in lignin convert to CH_3SH, a mercaptan gas by the impact of HS^+ ions. If the volatile gas escapes, the characteristic disgusting odor of a pulp mill can be smelt. On the other hand, OH^- ions – in collaboration with HS^- ions – break the chains of the lignin molecules and release phenolates. Keeping the pulp at pH 14, sulfur is bound to the breaks of the lignin molecules. It is pivotal to keep the pulp at a very high pH to prevent lignin from repolymerization (Kocurek 1989).

Most modern pulp mills use continuous digesters lined with stainless steel. Batch digesters are still used in older mills. The used cooking medium, called *black liquor*, contains the dissolved parts of wood (lignin, hemicelluloses, and extractable chemicals), in addition to sodium and sulfur chemicals. The organic residuals in *black liquor* are a valuable source for energy and recycling. Products like turpentine and colophony can be extracted from *black liquor* (Karlberg 1991). Turpentine and tall oil are by-products of the pulping process. When chips from certain species of trees are digested, fatty and resin acids, alcohols, and phytosterols are released and rise to the top of the vats. This material is known as tall oil because of its white, frothy appearance. It is sold for use as a fuel additive, dust control agent, road stabilizer, pavement binder, and roofing flux. Pulping of trees that contain large amounts of resin will produce sodium soaps. These soaps are collected from the *black liquor*. Gases from digesters and condensate from black liquor are processed to produce turpentine (Purssell 2010).

The recovery process aims at saving the inorganic chemical products in black liquor, using the energy source formed by organic materials and minimizing the environmental effects of the pulping process. The *black liquor* is concentrated in evaporators until it contains less than 40% water. The concentrated *black liquor* is incinerated, and sodium sulfate is added to replace the lost sodium chemicals. The combustion heat melts the inorganic chemicals which are then recovered from the bottom of the boiler. Dissolved in water, they form *green liquor* which contains sodium sulfide, sodium carbonate, and sodium sulfate. *Green liquor* is finally sent to a recausticizing plant, where it is treated with slacked lime to form *white liquor* and calcium carbonate. The *white liquor* is filtered and reused. Calcium carbonate is finally converted back to calcium oxide in a limekiln.

The recovery process is a major source of chemical exposure in pulp mills, especially with regard to volatile sulfur compounds, such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. However, in modern pulp mills, volatile sulfur compounds emerging from the pulping and recovery processes are collected and burned to reduce workplace exposure and pollution of the environment.

5 Sulfite Pulping

Sulfite pulping was the most common method of pulping until the mid-1900s, but it now accounts for a much smaller portion of industrial pulp production. It is a suitable method for cellulose production from spruce wood, e.g., in Germany. In the sulfite pulping process, a liquor of sulfurous acid (H_2SO_3) and bisulfate (HSO_3^-) is produced on-site. Elemental sulfur is burned to produce sulfur dioxide (SO_2). The sulfur dioxide is sent to an absorption tower and treated with one of four alkaline substances, calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$), ammonium hydroxide (NH_4OH), or the original sulfite base to the liquor. Sulfite pulping usually uses brick-lined batch digesters. The spent digestion mixture is called red liquor. In most processes, spent liquor is burned to produce heat. During this process, chemical recovery occurs (Smook 1989). Unbleached cellulose from sulfite pulping is used for transparent and fat-resistant paper. The density of cellulose made by sulfite pulping is lower than the density of products derived from sulfate pulping.

6 Pulp Bleaching

After pulps are produced, they are bleached in a multistage process to brighten them. This avoids brownish stains due to lignin in the final product. Bleaching can be done either by removing residual lignin from the pulp or by retaining it. Currently, in many bleaching procedures, chlorine dioxide is used instead of elemental chlorine as the first stage of the process. As it is difficult to transport, chlorine dioxide is usually generated on-site, using several different methods, the most common of which being acid treatment of sodium chlorate. Sodium hypochloride is produced by combining chlorine gas with sodium hydroxide. Completely chlorine-free bleaching procedures have been developed for environmental reasons. These utilize chelation and chelating agents, enzymes – usually xylanase – oxygen, ozone, per-acids, and hydrogen peroxide (Torén and Blanc 1997). In some processes, the lignin is not removed in the bleaching process. This is usually the case with pulps containing large amounts of lignin such as mechanical, ground-wood, and neutral sulfite semi-chemical pulps. In these cases, either reductive or oxidative chemicals are used for pulp brightening. Sodium dithionite is the most common reductive chemical in use today, and peroxides are commonly used if the process is oxidative. When chemo-thermo-mechanical pulp is bleached, additional chemicals such as sodium silicate or DTPA (diethylene triamine pentaacetic acid) are also used.

7 Paper and Cardboard Manufacture

There are no clear definitions of paper or cardboard. Thick paper is called cardboard, the sheet usually being over 0.3-mm thick and the weight of the material over 140 g/m^2. At present, there are more than 3000 different specialty papers, each serving a particular purpose. These may be very common ones, familiar for commodity papers, but more pronounced or with a closer tolerance. Such characteristics include strength, thickness, porosity, stiffness, abrasion resistance, and absorption. They may also have very specific characteristics, such as electrical conductivity, pore size distribution, resistance to certain chemicals, light and heat, chemical reactivity, and cleanliness.

The production of paper begins in pulpers, where chemical or mechanical pulp fibers are mixed with water in order to form a slurry. The fibers are then modified mechanically in beaters or refiners to provide more favorable conditions for bonding. Several chemicals are added to the fiber slurry in the stock-preparation phase to improve the properties of the final product. Acids or bases may be used for pH adjustment. Sizing agents control the penetration of liquids, and they are added either at the wet end of the paper machine or applied to the surface of the paper in the machine. Rosin is a typical sizing agent; it is usually precipitated onto the fibers with the help of aluminum sulfate. Wax or synthetic sizing agents, such as epoxides, may also be used.

In order to improve the physical properties of paper, especially strength and resistance to erasure, natural polymers such as starches and gums are added to the stock, as well as cellulose compounds, such as carboxymethyl cellulose, or synthetic polymers, e.g., polyacrylamides and polyamines. Wet-strength resins, such as polyamide resins, may also be added to the stock. Urea-formaldehyde and melamine-formaldehyde resins are no longer widely used for improving wet strength. Mineral fillers are used to improve the physical and optical properties of paper. They usually comprise 5–15% of the weight and can comprise more than 30% in some paper grades. The most common fillers are clay (kaolin), calcium carbonate, talc, and titanium dioxide. Different dyes and pigments are added to the stock in order to color the paper. Basic dyes are in most abundant use today, but acidic and direct dyes are also applied. Retention-aid chemicals may be added, as well as defoamers (e.g., fatty-acid compounds), pitch-control agents, optical brighteners (usually stilbene derivates) and, in some cases, fiber deflocculants.

Different microbes, such as bacteria, yeast, mold, fungal spores (mainly myxomycetae), protozoae, and algae, find a suitable culture medium in the pulp. They produce slime that may spoil the quality of the produced paper by staining. This may even be enhanced by recovery techniques. Therefore, various slimicides are added to the stock for microbe control. All biocides used as slimicides are irritants; most of them can also cause allergic contact dermatitis (see Table 1).

The prepared fiber stock is made into paper or cardboard by Fourdrinier paper machines. First, the prepared stock containing approximately 0.2–1.5% of solid material flows via the stock inlet or flow spreader into a pressurized head box. From there, the stock is distributed evenly onto a moving wire. On this moving, endless wire made of plastic polymers, the paper sheet is formed by two simultaneous processes. Water is drained away through gravity and vacuum suction and fiber orientation under turbulence forms fiber networks. In the press section, additional water is removed from the paper sheet by running it through press rolls. In the dryer section, most of the water remaining in the fiber web is evaporated as the sheet is run over steam-heated cylinders. Further fiber bonding happens at the same time. In the calender section, the thickness of the paper sheet may be reduced and its surface smoothened by pressing the sheet between metal cylinders. The paper is wound onto a reel. The full-width machine reel is then transferred to a winder to cut and rewind it into rolls of suitable size according to the customer's needs. Finally, the rolls are wrapped for delivery.

Surface sizing can be done as part of the process in sizing presses. The most common sizing material is starch, occasionally with added wax or resin compounds. Sometimes, sizing is performed during the calendering phase or even in special tubs. The paper is often coated to improve the printing and other qualities of the paper surface. The coating can be done either in or out of the machine, using different coating components. Mineral pigments, such as clay or precipitated calcium carbonate, are the most common coating agents. Titanium dioxide or plastic components may also be used. The coating pigments are mixed with different adhesives and additives. The adhesives are either water soluble, such as glues, starches, gums and casein, or polymers, such as latexes, acrylics (Matura et al. 1995), and polyvinyl acetates. Depending upon the paper quality, various types of coating additives are used, such as water-proofing agents, plasticizers, thickeners, dispersants, preservatives, and dyes.

8 Waste Paper

Waste paper is a crucial raw material for the paper industry, comprising approximately 50% of all raw materials. It is incubated in warm water, cleaned mechanically, and torn into pieces.

This pulp undergoes a de-inking process in an alkaline solution (pH 10–11) in order to eliminate dyes and fillers. Hydrogen peroxide is added to prevent pulp from turning yellow. Added air bubbles and other de-inking chemicals like fatty acids force the residual particles of dyes to accumulate as a foam on the surface of the pulp which has to be removed. After neutralizing with sulfuric acid, the pulp enters the bleaching process as described above (Borchardt 1997).

9 Irritants

Acids
Alkalis
Ammonia
Bleaching agents (chlorine gas, chlorine dioxide, sodium hydroxide, sodium hypochlorite, ozone, hydrogen peroxide)
Heat and humidity
Soaps and detergents
Solvents
Sulfur dioxide
Water (wet work)

10 Standard Allergens

Carba mix, 3% pet (rubber, gloves)
Cobalt chloride, 1% pet
Colophony (rosin), 20% pet
1,2-dibromo-2,4-dicyanobutane, 0.2 pet
Epoxy resin, 1% pet
Ethylenediamine dihydrochloride, 1% pet
Formaldehyde, 1% aq (preservative)
Fragrance mix, 8% pet (moist toilet paper)
Lanolin (anhydrous), as is (lubricant)
2-Mercaptobenzothiazole, 1% pet (rubber, slimicides)
Mercapto mix, 1% pet (rubber, gloves)
Methylchloroisothiazolinone/methylisothiazolinone (= MCI/MI = Kathon™ CG), 0.01% aq (preservative in moist toilet paper and sanitary wipes)
Nickel sulfate, 5% pet (tools)
Potassium dichromate, 0.5% pet (sulfate pulp)
4-Phenylenediamine, 1% (rubber)
Thiuram mix, 1% pet (rubber)

11 Additional Allergens

P-Aminoazobenzene, 0.25% pet (azo dyes)
P-aminophenol, 1% pet (dyes)
Anthraquinone, 2% pet (catalyst in delignification reactions; photosensitizer)
2-Bromo-4′-hydroxyacetophenone, 0.1% aq (used as slimicide)
Benzophenone, 1% pet (UV-light inhibitor)
4-tertiary butyl catechol 0.5% pet (thermofax paper)
Casein (type-I and type-IV allergy)
4-Diethylaminobenzene diazonium chloride (DDA), 10% aq (copy paper)
Dichlorophene, 1% pet (germicidal agent for slime control).
2,3-Epoxypropyl trimethyl ammonium chloride, 0.5% pet (added to increase strength of paper for surface sizing)

Table 1 Slimicides in the pulp and paper industry (Geier and Lessmann 2006/2001)

Substance	CAS number	References
Mercaptobenzothiazole	149-30-4, 2492-26-4	Fregert 1976
(2-Benzothiazolylthio)methyl thiocyanate	21564-17-0	Fregert 1976
Disodium cyanodithiocarbamate	138-93-2	Fregert 1976
Potassium *N*-hydroxymethyl-*N*-methyldithiocarbamate	51026-28-9	Fregert 1976
Potassium methyldithiocarbamate	137-41-7	Fregert 1976
Sodium dimethyldithiocarbamate	128-04-1	Fregert 1976
Disodium ethylenebis(dithiocarbamate)	142-59-6	Fregert 1976
Methylene-bis-thiocyanate	6317-18-6	Andersen and Hamann 1983; Jäppinen and Eskelinen 1987
2-Hydroxypropylmethanethiosulfonate	30388-01-3	Fregert 1976
Tetrahydro-3,5-dimethyl-2 H-1,3,5-thiadiazine-2-thione (= Dazomet; DMTT; Mylone; Thiazone)	533-74-4	Fregert 1976
2-Butene-1,4-diyl bis(bromoacetate)	20679-58-7	Fregert 1976; Rycroft and Calnan 1980; Shehade et al. 1990
2,2-Dibromo-2-cyanoacetamide	10222-01-2	Shehade et al. 1990
N,4-Dihydroxy-alpha-oxobenzeneacetimidoyl chloride	34911-46-1	Fregert 1976; Ahrens and Jöckel 1996
2-Bromo-4-hydroxy acetophenone	2491-38-5	Fregert 1976; Jensen and Andersen 2003
2-Bromo-2-nitroethenyl benzene	7166-19-0	Ahrens and Jöckel 1996
2-Bromo-2-nitro-1,3-propanediol (= Bronopol)	52-51-7	Fregert 1976
2-(Hydroxymethyl)-2-nitropropane-1,3-diol	126-11-4	Ahrens and Jöckel 1996
4-Bromo-2,3-dichlorotetrahydrothiophene-1,1-dioxide	65243-01-8	Rycroft and Calnan 1980
Methylchloroisothiazolinone/ methylisothiazolinone (= MCI/MI, Kathon CG, Kathon WT)	26172-55-4, 2682-20-4	Shehade et al. 1990; Ahrens and Jöckel 1996; Torén et al. 1997; Kujala and Niinimäki 1999; Majamaa et al. 1999
2-Octyl-3(2 H)-isothiazolinone (Kathon 893)	26530-20-1	Shehade et al. 1990
8-Hydroxyquinoline	148-24-3	Ahrens and Jöckel 1996
Glutardialdehyde (= glutaraldehyde, Pentanedial)	111-30-8	Ahrens and Jöckel 1996; Shehade et al. 1990

Glutaraldehyde, 0.2% pet (used as slimicide)
Hydroquinone, 1% pet (antioxidant)
Iodopropynyl butyl carbamate, 0.2% pet (moist sanitary wipes)
Melamine-formaldehyde, 7% pet
Methyl gallate, 2% pet (thermofax paper)
Methylisothiazolinone, 0.05 aq
Methyl methacrylate, 2% pet (and other acrylics in resin emulsions)
Nigrosine™, 1% pet
Paper, 10% acetone
Phenol-formaldehyde resin, 10% pet (used in plywood and adhesives for paper)
Phenylmercuric acetate, 0.01% aq (germicidal agent)
Phenylmercuric nitrate, 0.05% pet (germicidal agent)
o-Phenylphenol, 1% pet (germicidal agent)

Resorcinol-formaldehyde resin, 5% pet (adhesives used in plywood and paper)
Slimicides (see Table 1)
Sodium metabisulfite, 1% aq (pulping process)
Thiourea, 0.1% pet (copy paper)
Tricresyl phosphate, 2% pet (carbon paper)
Urea-formaldehyde, 10% pet
Xylanase (type-I and type-IV allergy)

12 Specific Aspects

Workers in the pulp and paper industry may be exposed to a variety of chemical products. However, production occurs in enclosed machinery. Many steps in modern paper and pulp processing are automated. Operating personnel spend most of their time in control rooms, away from the industrial process. However, maintenance staff may be exposed during repair processes. Exposure to hazardous substances may happen accidentally, during service or due to malfunction. Accidental gassings may not be detected by shift-long average-based sampling devices. Continuous monitoring and data logging are necessary to recognize and fully characterize these exposures.

13 Toxic Agents

The International Agency for Research on Cancer (IARC) has conducted a multinational study on possible cancer risks in the pulp and paper industry (Kauppinen et al. 1997). To this end, an exposure database has been collected. This database includes 31,502 measurements of 246 different chemical agents, submitted from 13 countries. The concentration of a variety of agents, including sulfur dioxide, chlorine dioxide, carbon monoxide, nitrogen dioxide, ozone, ammonia, and formaldehyde, may, at times, exceed current permissible occupational exposure limits. Sulfur dioxide exposures occur primarily in association with the digestion of sulfite pulp, the manufacture of sulfite cooking liquor, and the bleaching of sulfite pulp. Exposures may also occur in the recovery of sulfate pulp. In the IARC study, 38% of sulfur dioxide levels exceeded the 8-h time-weighted average concentration. Chlorine, chlorine dioxide, and sulfur dioxide are irritant gases. Workers in the bleaching plants of pulp mills that report gassing incidents have an increased incidence of respiratory symptoms and airway obstruction. Bronchoconstriction occurs at lower concentrations of sulfur dioxide in individuals who are exerting themselves and in those with hyperresponsive airways (Anderson et al. 1974). Workers exposed to high levels of sulfur dioxide in a sulfite mill in Norway were found to have an excess of respiratory symptoms and abnormally low airflow measurements (Skalpe 1964). An exposure to 1–2.5 ppm of sulfur dioxide in a smelter was associated with an increase in respiratory symptoms and excessive yearly loss of forced expiratory volume (Smith et al. 1977). Reduced sulfur gases are produced in sulfate (kraft) pulping and pulp recovery. The most common reduced sulfur gas is hydrogen sulfide (H_2S). Hydrogen sulfide gas is produced if black liquor comes in contact with acids in sewer water. In the database, only 2% of hydrogen sulfide measurements exceeded the time-weighted average concentration. Hydrogen sulfide has an odor of rotten eggs, with local irritative effects. Signs of ocular imitation occur at levels above 50 ppm and include ocular pain, keratitis, photophobia, blepharospasm, cough, sore throat, vomiting, and nausea.

Workers in the wood processing and chipping areas of pulp mills may be exposed to wood dust. Excessive levels of organic dust may be found in soft paper mills. In addition, various fertilizers, insecticides, herbicides, and fungicides are used in the forestry industry. Organophosphate or carbamate insecticide applications are used to control insects such as bark beetles and budworms. Commonly used herbicides include glyphosphate and hexazinone. BTK (*Bacillus thuringiensis* var. *kurstaki*) is a microorganism used in insect control, producing a substance that is toxic to caterpillars. IgE-mediated allergic reactions to BTK have been described. Outdoor workers may be exposed to these compounds (Purssell 2010).

High concentrations of formaldehyde, perchloroethylene, and ammonia may occur in the calendering and on-machine coating areas of paper mills. Formaldehyde and formaldehyde releasers are used to improve the wet-strength water-resistance, shrink-resistance, grease-resistance, and other characteristics of paper and paper products. Furthermore, formaldehyde serves as a disinfectant and preservative in paper manufacture and in the preparation of finishes, sizing agents, and parchment paper. High levels of formaldehyde were detected at the dry section of the manufacturing process where this compound was released from resins into the air (Ahrens and Jöckel 1996).

14 Physical Hazards

Noise is a common and pervasive hazard in many pulp mills. Noise levels exceeding 85 dBA occur in 75% of pulp and paper plants. The risk of noise exposure has been reduced by enclosed control rooms and appropriate protection. Heat and humidity are also hazards. In some areas, workers may be exposed to extremes of temperature.

15 Cancer

Epidemiological studies showed an increased risk of lung, stomach, rectal, and prostate cancer, malignant mesothelioma and hematologic malignancies, both lymphoma and leukemia, among workers in the pulp and paper industry (Jäppinen et al. 1987; Torén et al. 1991, 1996; Matanoski et al. 1998; Band et al. 2001; Andersson et al. 2010). These findings may be associated with exposure to wood dust, terpenes, extractable wood compounds, or chlorinated organic by-products (Torén et al. 1991, 1996). According to the IARC (Kauppinen et al. 1997), various substances at the workplaces in the pulp and paper industry are possible human carcinogens, e.g., benzodine-based dyes, formaldehyde, and epichlorohydrin which are used as paper additives. Many pipes and vessels are made of stainless steel. Exposure to hexavalent chromium and nickel compounds can occur when steel is welded. Other carcinogens can be calcium oxide fumes, sulfur dioxide, sulfuric acid mists, benzene, diesel exhausts, hydrazine, styrene, mineral oils, chlorinated phenols, and dioxins.

16 Irritant and Allergic Contact Dermatitis

Contact dermatitis is a rare disease among pulp and paper workers. More than 600 products are used in the manufacture of different paper grades from the cellulose fibers of trees. The products include fillers, preservatives, plasticizers, bleaching agents, chelators, adhesives, dispersing agents, corrosion inhibitors, and many other additives (Fregert 1976). Even though paper-factory workers were exposed to an array of organic and inorganic compounds, only 1.3% of them suffered from work-related dermatitis in a Swedish wood-pulp factory (Efskind 1980).

In contrast, contact dermatitis was found by Jungbauer et al. (2005) in 26% of Dutch paper-mill workers. The authors performed a cross-sectional study among 80 paper-mill workers having daily exposure to skin irritants and allergens. All the workers completed a questionnaire and underwent a standard interview and physical examination. Workers whose history indicated possible contact allergy were patch-tested and prick-tested. They reported a high exposure to skin irritants, especially when performing tasks that caused the hands and feet to become wet from sweating and having contact with process water. Atopic dermatitis was seen in 3% of the workers. Irritant contact dermatitis was seen in 26% of the workers and 36% were diagnosed with mycosis of the feet. All cases of contact dermatitis and mycosis could be attributed to occupational exposure to skin irritants and to occlusive clothing, e.g., safety shoes. Jungbauer et al. (2005) did not detect a single case of allergic contact dermatitis. Wet work may be problem at several workplaces. Wearing suitable gloves can prevent irritant contact dermatitis. To conclude, occupational dermatitis in paper mills is primarily related to exposure to skin irritants.

Meding et al. (1993) did not find an increased prevalence of contact dermatitis in Swedish paper-mill workers, although pruritus and skin irritation related to paper dust were observed. Cases of colophony allergy among workers in paper mills were rare (Meding et al. 1993). The actual handling of paper in paper mills is not as frequent as in office work, since very little work is performed manually. Torén (1989) found no reports indicating that paper dust would cause skin problems, but an increased prevalence of asthma and chronic obstructive pulmonary disease was evident from the literature.

Paper strength is increased by the adding cationic starch to the pulp. The manufacture of this type of starch involves a quaternium ammonium compound known as 2,3-epoxypropyl trimethyl ammonium chloride, also known as glycidyl trimethyl ammonium chloride. This proved a potent sensitizer in guinea pigs and sensitized several Finnish workers exposed to it occupationally. A patch test concentration of 0.5% pet was effective in identifying the cases (Estlander et al. 1997). Xylanase and other enzymes provoked both contact urticaria in an airborne pattern and respiratory symptoms (Tarvainen et al. 1991).

Roselino et al. (1996) observed a high number of alopecia areata cases among workers in a Brazilian paper mill. Toxicologic evaluation revealed an acrylamide-like substance in the workers; they had been exposed to mist containing acrylamide in the pulp-pressing room.

Slimicides are the major source for allergic contact dermatitis among pulp and paper workers (see *Table* 1). They contain biocides which are well known as potent irritants and allergens (Fregert 1976; Ahrens and Jöckel 1996; Shehade et al. 1990). The low prevalence of contact dermatitis (Rycroft and Calnan 1980; Torén et al. 1997) is explained by the fact that the workers do not come into contact with these substances when performing standard procedures. Rycroft and Calnan (1980) reported dermatitis from slimicides in a paper mill, but it was not possible to decide whether these patch test reactions were allergic or irritant. Slimicides are added to the pulp in excessively high concentrations, such as CMI/MI in an aqueous solution of 1–2% (= 10,000–20,000 ppm). The accidental exposure of the skin results in irritant lesions and immediate sensitization (Kujala and Niinimäki 1999). Torén et al. (1997) reported two cases of contact allergy to methylisothiazolinones. One patient worked as a batcher in a paper mill, the other as an agent for a company marketing slimicides. Both patients were in charge of pumping slimicides containing methylisothiazolinones. During pumping, the liquid often overflowed, and their clothes were wet with slimicides. Both individuals suffered from dermatitis, which improved when they were away from work. A clinical investigation confirmed the dermatitis diagnosis, and positive patch tests to Kathon CG were found. Both workers were exposed to extraordinarily high concentrations of methylisothiazolinones that caused sensitization. Such conditions could also provoke contact dermatitis in an airborne pattern without direct skin contact (Majamaa et al. 1999). Jäppinen and Eskelinen (1987) patch-tested 34 workers exposed to the slimicide methylene-bis-thiocyanate, but no allergic patch test reactions were observed. Jensen and Anderson (2003) reported a case of allergic contact dermatitis from a paper-mill slimicide containing 2-bromo-4′-hydroxyacetophenone. Since 2003, no further reports about hazardous slimicides have been published. The new safety measures have probably solved this problem.

17 Paper Dermatitis

Paper has become a ubiquitous material of everyday life. Allergic contact dermatitis caused by paper does occur, but it is very rare. The frequency of paper dermatitis in the total population is low and has been reported to represent 0.8% of all occupational dermatitis (Wikström 1969). Patch tests with paper as is are usually negative. An appropriate patch test extract is prepared from an acetone extract of paper at 10% concentration (Karlberg and Lidén 1992).

18 Colophony (Rosin)

Hand eczema due to colophony can occur from handling paper and newsprint (Bergmark and Meding 1983; Lidén and Karlberg 1992). Colophony is a complex mixture of resin acids (about 90%) and neural substances, i.e., diterpene alcohols, aldehydes, and hydrocarbons (about 10%). Its composition varies with the species from which it is obtained and also depends on the recovery processes and storage conditions. The acids are diterpenoid acids, of which the abietane- and pimarane-type structures are the most abundant. The most potent sensitizer among the colophony constituents is maleopimaric acid (Karlberg et al. 1990). Air oxidation increases the allergenic potential of tall-oil rosin (Karlberg 1991). The content of colophony in paper and paper products was investigated. "Environmentally friendly paper" of mechanical pulp from coniferous wood contained more colophony components than paper based on chemical pulp (Karlberg et al. 1995). In colophony-sensitive subjects, a higher response was seen to unprinted paper of mechanical pulps than to paper based on chemical pulps, since the extractive material containing the colophony components was not separated from the mechanical pulp. The use of cotton gloves when in contact with paper might alleviate the dermatitis (Karlberg and Lidén 1992).

Bergh et al. (1994) discovered colophony in paper-based surgical clothing as a source for occupational allergic contact dermatitis among nursing staff. Pereira et al. (1997) detected colophony in lottery tickets that caused allergic contact dermatitis. Allergic contact dermatitis from cigarettes may be due to colophony and formaldehyde in cigarette paper (Glick et al. 2009). Wikström (1969) reported that – in dermatitis due to typewriting paper – the allergen appeared to occur in the "sizing" contained in the paper, a gum resin that consists partly of colophony. Sensitivity to the typewriting paper can also be accompanied by sensitivity to colophony, juniper tar, and Styrax. All of these substances contain mixtures of resinous acids, one of which is abietic acid.

Thermosensitive telefax paper contains a base paper and a thermosensitive color-forming layer. Kanerva et al. (1992) reported occupational allergic contact dermatitis caused by colophony in telefax paper. Hand dermatitis that improved on job leave and during vacation and then relapsed when the patient returned to work was attributed to colophony in telefax paper containing 1% colophony. Patch testing with this fax paper gave only partial reactivity (Kanerva et al. 1992).

19 Formaldehyde and Formaldehyde Resins

Many types of paper, e.g., glossy table paper, contain formaldehyde or its resin to increase wet strength and to avoid mildew. Shiny, heavy, more expensive table paper is much more likely to contain formaldehyde than the thinner, less expensive, duller, more fragile type of paper. The handling of most newspapers, magazines, both hardcover and paperback books, and glossy paper readily produces dermatitis in formaldehyde-sensitive individuals. Paper towels may contain melamine-formaldehyde resin to increase resistance to water, and paper money may contain formaldehyde and its resins to prevent it from mildewing (Fisher 1976). Wrapping paper, inexpensive paper, and newspapers may produce dermatitis from the presence of free formaldehyde (Fregert 1974). An occupational dermatitis due to formaldehyde in newspaper was reported by Sanchez et al. (1997). Black (1971) reported a formaldehyde-sensitive individual who was allergic to blank newsprint. The estimation of free formaldehyde content of the newsprint turned out to be 0.02%. Paper towels used in Black's hospital contained 0.03% formaldehyde.

Jordan and Bourlas (1975) reported typewriter correction paper to contain phenol-formaldehyde resin. The resin is in use as a binder for the boundary coating on the paper. Patch testing should be performed with the powdered side of the paper (Malten and Seutter 1984). Formaldehyde and quaternium-15 in a photocopier toner caused an allergic contact dermatitis (Zina et al. 2000). Zussman (1987) reported a bank teller who had an allergic patch test reaction to formaldehyde. Formaldehyde resin was found to have been used in the processing of the paper currency. Paper money applied to his palmar surfaces caused a recurrence of vesicles, itching, and dermatitis. Koch also reported a case of hand dermatitis due to formaldehyde and colophony in banknotes (1995). The formaldehyde-sensitive patient also acquires dermatitis from many types of paper tissues, paper plates, and cups. He cannot tolerate any art paper used for acrylic paint or watercolors. Formaldehyde is present in the lubricants used to keep cardboard from wrinkling during its manufacture (Rietschel and Fowler 2008).

20 Carbon Paper

Carbon paper is made by coating very lightweight paper stock with a mixture of pigments and medium. A carbon paper ink basically consists of three elements: waxes (beeswax, carde lilla, carnauba, montan, oricony, paraffinwax), oils (mineral and castor oils, stearic and oleic acids), and colors (carbon black, methyl and crystal violet, miliori blue, nigrosine, Victoria blue). The oils are nondrying to produce softness and compactness of the ink. The waxes keep the ink hard and dry at room temperature and are a vehicle for the colors. The quality of the paper on which the ink is deposited is also important because it must be thin and free of pinholes (Carver 1942). Hjorth described a patient with a positive patch test to one type of carbon paper and to the plasticizer triphenyl phosphate, which was present at a concentration of 30% in the film emulsion. Calnan and Connor (1972) reported a case of contact dermatitis from nigrosine, which was present only in a special carbon paper used for computer work. Another contact allergen causing carbon paper dermatitis was methyl violet (Calnan 1974).

21 Carbonless Copy Paper (NCR Paper)

Calnan (1981) described carbonless copy paper – or no carbon required (NCR) paper – as pressure-sensitive paper for which either a ballpoint pen or an electric typewriter was the most suitable writing instrument. Carbonless copy paper has largely eliminated the use of carbon paper. With the dominance of word processors and nonimpact printers over typewriting, carbon copies have almost disappeared from use in correspondence. The principle was originally covered by a patent owned by National Cash Register (NCR) which then gave the name NCR (no carbon required). After the patent expired, the NCR principle was widely copied, and carbonless copy paper developed into a commodity with many suppliers. To create carbonless copy paper, an emulsion of oil-carried color former is encapsulated in microcapsules and applied as a coating on the backside of the copying paper. Through the pressure of writing, the microcapsules are broken, and the color former solution flows to wet the front side coating of a receiving sheet, i.e., the front side coating reacts with the color former to form an image. The “inks” are “color formers” that are colorless at 1 pH and colored at another. The pH inside the capsules is acidic, and the pH outside the capsules is alkaline. The top surface of the second sheet is coated with a material which absorbs the color former when the microcapsules are broken by the pressure of the ballpoint pen. This material is alkaline, and thus, the color is created.

The color formers are mostly triphenyl methane dyes, such as gentian violet and malachite green, which are dissolved in organic solvents inside the microcapsules. The solvents include kerosene diarylethanes, alkyl naphthalenes, cyclohexane, and dibutyl phthalate, which may be diluted with odorless kerosene. Some of these papers contain formaldehyde; others contain ammonia.

Carbonless copy paper, introduced in 1954, is ubiquitous in offices, and because of this, many workers and clients come in contact with it. Its safety to workers who handle large amounts of NCR paper has been addressed in numerous studies and reports (Kendrick 1958). Consistently, NCR paper in US commerce since 1987 has produced neither primary skin irritation nor skin sensitization under exaggerated test conditions. Years after the introduction of carbonless copy paper, the first case reports appeared in 1974, suggesting an association between its use and various generic symptoms. Most of the earliest reports occurred in Sweden in response to negative publicity concerning the product, and to date approximately half of all published articles originate in Scandinavia (Norbäck et al. 1988; Buring and Hennekens 1991; Omland et al. 1993). Many early reports were questionnaire/interview studies which suffered from suggestive questions, biases, and lack of control for confounding factors. Few studies included a comparison group making it impossible to estimate risk values. Later, "sick building syndrome" studies, accounting for many relevant factors in the office environment, found no association between exposure to carbonless copy paper and symptoms unexplained by other factors. A few reports of symptoms have emanated from printing facilities (with a multiplicity of other chemical exposures), but generally most symptoms were reported in the office setting where the exposure was lower than in the manufacturing or printing settings. The National Institute for Occupational Safety and Health (NIOSH) evaluated the literature as to possible health hazards to health posed by carbonless copy paper, and concluded that it is not a hazard to workers and has only a small possibility of producing mild and transient skin irritation (Graves et al. 2000).

Carbonless copy paper (NCR) was incriminated as the cause of numerous symptoms: itching, redness of the skin, upper respiratory symptoms, hoarseness, airway obstruction, chest tightness and pain, asthma, fatigue, nausea, headache, rapid heartbeat, and burning of the nose, eyes, mouth, and chest (Murray 1991). On rare occasions, immediate (Hannuksela and Björksten 1989) or delayed allergic reactions (Marks 1981; Shehade et al. 1987; Kanerva et al. 1993) had been detected. Rycroft and Calnan (1979) stated that there had been several instances of irritation of the skin, eyes, and upper respiratory tract in office workers handling carbonless copy paper. Symptoms described by them were initially dismissed by some physicians as psychoneurotic. The symptoms were suggestive of an airborne irritant. The most likely candidates for the cause of these irritant symptoms resided among a variety of organic solvents that were an essential component of these systems. However, exposure to the constituents of the NCR paper during its manufacture is considerably greater than in its use, and until now, no such cases have been reported. Some people in Europe refused the work with carbonless copy paper; concern was expressed in the European Parliament in view of its undoubted convenience and superiority over carbon paper. Murray (1991) was asked by the Commission of the European Communities for a report based on visits to manufacturers and users and the investigation of complaints. According to Murray (1991), the complaints were more likely attributable to "sick building syndrome" than to the specific effect of any component of the paper.

There are very few case reports concerning skin and respiratory symptoms due to NCR paper. Airborne irritant contact dermatitis caused by volatile ingredients released into the air by NCR paper was reported by Calnan 1979; Menné et al. 1981, and Murray 1991. Office workers suffered from respiratory symptoms attributed in part to formaldehyde which had been released from carbonless copy paper (Gockel et al. 1981), but other researchers were unable to replicate this finding (Marks et al. 1984; Murray 1991). Menné et al.'s (1981) epidemiological investigation failed to reveal any connection between office workers' health complaints and ventilation, temperature, or humidity.

NCR-paper-induced contact urticaria (Hannuksela and Björksten 1989) accompanied by eye, throat, and respiratory symptoms was attributed to prostaglandin release (Marks et al. 1984). A 27-year-old woman experienced pruritus, eye and throat irritation, hoarseness, shortness of breath, and fatigue within half an hour of exposure to carbonless copy paper. On two separate occasions, she was purposely challenged in a controlled-blinded fashion with portions of this type of paper. This resulted on both occasions in contact urticaria of the hand that held the paper and changes in pulmonary function flow-volume loops (Marks et al. 1984). LaMarte et al. (1984) reported on two patients who had recurrent episodes of hoarseness, cough, flushing, pruritus, and rash occurring within 30 min of topical exposure to carbonless copy paper. When one of the chemical ingredients in the paper, alkylphenol-novolak-resin, was applied to the arms, two patients experienced hoarseness and angioedema of the arms which corresponded to contact urticaria. The authors also documented laryngeal edema and an increase of plasma histamine levels in one patient after challenging.

Marks (1981) reported an allergic reaction to a component of carbonless paper containing a color former composed of paratoluene sulfinate of Michler's hydrol (PTSMH). This component is a colorless dye salt that forms a colored print on transfer to a suitable receiving paper. The reaction of Michler's hydrol and paratoluene sulfinic acid produces PTSMH. This chemical coating was developed to improve business copy papers. Shehade et al. (1987) reported a case of allergic contact dermatitis to crystal violet lactone, a triaryl methane derivate contained in NCR paper. A fork-lift operator was sensitized to azo dyes while collecting used color-containers in a factory producing NCR paper (Smith et al. 1999). Kanerva et al. (1990) reported on a 43-year-old machinist whose work involved the manufacture of NCR paper and who developed occupational dermatitis on the hands. Performing patch tests with both the NCR paper and diethylenetriamine (DETA), one of the chemicals used to produce the microcapsules of the NCR paper, provoked allergic reactions.

22 Copy Paper

According to Rietschel and Fowler (2008), there are four methods of copying or duplicating:

1. *Verifax* (Eastman Kodak)
2. Diazo or dyeline process
3. *Thermofax* (heat process)
4. The electrostatic or *xerographic* method

22.1 *Verifax* (Eastman Kodak): Is Seldom Used

This is a photocopying method which was popular in the 1970s and 1980s of the twentieth century. Two men were sensitized while employed making the powder for the sensitized emulsion. Both men developed severe and widespread eczema and were sensitized by 4-phenyl catechol, patch-tested with 0.5% pet (Harman and Sarkany 1960). Jensen and Roed-Petersen (1979) described patients who had itchy erythema of the face and headaches from vapor released from wet toners used in photocopy machines, but they were unable to identify the precise chemical. Adequate ventilation solved the problem.

22.2 Diazo or Dyeline Process

Engineering drawings are often duplicated as light prints, using diazonium process. An original pattern is placed on diazo-sensitized paper and is exposed to UV light. The UV light decomposes the diazonium salts in the diazo paper, except where they are shielded by the pattern. Gaseous nitrogen evaporates from this composition as a reaction to UV light. Colorless aminophenol stays on the exposed paper. This chemical reaction does not affect the pattern under which the diazonium compound is not transformed. It is converted into diazonium dye in the next step (Geier and Fuchs 1993). Then the paper is developed with ammonia gas which causes a change of color in the unexposed portions of the diazo-sensitized paper. An irritant dermatitis may occur from the ammonia used in the process. Diazonium salts interact with "coupling agents" present in the paper to give a blue, black, or brown copy by the formation of azo dyes (Harman and Sarkany 1960).

The coupling agents are generally aromatic alcohols such as phenol and resorcinol derivates. Other components such as stabilizing agents are also present. Zinc chloride and acids such as citric acid inhibit chemical interactions at room temperature, thus preventing premature coupling. Nickel salts are present in some papers.

The allergen in diazo paper is usually 4-diethylaminobenzene diazonium chloride (diazodiethyl aniline hydrochloride, DDA), which is reduced to an amine that may cross-react with 4-phenylenediamine. Cross-reactions do not appear to occur with other azo compounds. DDA is not a sensitizer when it is irradiated. Thus, patch tests with the nonirradiated paper are positive in sensitized individuals, but are negative with irradiated paper (Gianotti and Meneghini 1966; Mijnssen and Verspyck 1967; Foussereau and Benezra 1970; Pambor and Poweleit 1992). 4-Dimethylaminobenzene diazonium chloride may also be present in diazo copy paper (Geier and Fuchs 1993). Most patients became sensitized while copying. There is only one case report about a man who developed an allergic contact dermatitis to 4-diazo-2-methyl-pyrrolidinobenzene at work while producing copy paper (Crijns et al. 1987).

Antioxidants, e.g., thiourea (= dimethyl thiourea), prevent yellowing of the white nonimage area. Dooms-Goossens et al. (1979) reported a textile cutter who had conjunctivitis and an erythematous itching dermatitis on her eyelids, nasal, mucous membranes, and the corners of her mouth. Patch testing revealed a strong positive reaction to the textile-cutting patterns which were duplicated by diazo processing. The airborne contact dermatitis was specifically caused by thiourea (= dimethyl thiourea), an additive in diazo-sensitized paper that prevents yellowing of diazo-sensitized paper (Dooms-Goossens et al. 1987). Sengel et al. (1979) and Kellett et al. (1984) reported similar cases. In addition to sensitization, thiourea may cause photodermatitis (Van der Leun et al. 1977; Geier and Fuchs 1993; Kanerva et al. 2000).

22.3 *Thermofax* (Heat Process)

This heat process is not only used in duplication paper, but also by cashiers producing sales slips as receipts in many different businesses. Allergic contact dermatitis due to 4-tertiary butyl catechol caused by *thermofax* paper has been reported since the 1950s (Fisher 1958; Hasegawa et al. 1958; Gaul 1960; Harman and Sarkany 1960; Kanerva et al. 1992). Dickel and Merk (1997) described a case of occupational relevance: A patient developed a sensitization to 4-tertiary butyl catechol to which he was exposed at his workplace. Degos et al. (1968) reported dermatitis due to methyl gallate, another antioxidant used in *thermofax* paper. Patch tests may be performed with the butyl catechol 0.5% pet, and methyl gallate 2% pet. The *thermofax* paper may be tested as is (Rietschel and Fowler 2008). There are several reports of *thermofax* dermatitis that stops when the sensitized person is no longer in contact with the duplication paper, or if he or she uses a different paper.

22.4 The Electrostatic or *Xerographic* Method

At this writing, no instance of contact dermatitis from this duplication process has been reported.

23 Toilet Paper

Recycled toilet paper may cause irritant contact dermatitis (Blecher and Korting 1995). Moist toilet paper – baby wipes and moist towelettes – contain sensitizing preservatives (Zoli et al. 2006), such as formaldehyde (Piletta-Zanin et al. 1998), MCI/MI (Minet et al. 1989; de Groot et al. 1991; Hulsmans et al. 1992; Blecher and Korting 1995; Guimaraens et al. 1996; Timmermans et al. 2007; Gardner et al. 2010), methylisothiazolinone (Garcia-Gavin and Goossens 2010). A case of anal and palmar contact dermatitis caused by iodopropynyl butyl carbamate in moist sanitary wipes was described by Schöllnast et al. (2003). Iodopropynyl butyl carbamate is increasingly used as preservative in common cosmetic formulations and moist sanitary wipes as a substitute for the frequently used sensitizers isothiazolinones and methyldibromoglutaronitrile (Marcano et al. 2007). A Bulgarian case report about moist skin wipes causing chronic dermatitis in the anogenital area was recently published (Kazandjieva et al. 2014). The sensitizing capacity of preservatives is a serious problem for the cosmetic industry, since hypoallergenic preservatives are not available, but products such as moist sanitary wipes in large packages definitely require protection from microbial contamination.

Perfumed facial tissues, toilet paper, and sanitary napkins can produce allergic contact dermatitis, particularly if they contain cinnamic aldehyde or cinnamic alcohol (Keith et al. 1969; Larsen 1979; Guin 1981). However, Parks (1969) believed that perfume in toilet tissue was unlikely to cause sensitivity because of its low concentration and the manufacturing practice of applying it to the inner core of the roll. The perfume is probably there in low concentration, since it has to be carried to the paper by diffusion.

24 Conclusion

Paper has played a vital role in the cultural development of mankind. It still has a key role in communication and is needed in many other fields of our society. There is no doubt that it will continue to be of great importance in the future. Paper must, however, maintain its competitiveness through continuous product development in order to meet the ever-increasing demands on its performance. It must also be produced economically by environment-friendly processes with the minimum use of resources. To meet these challenges, everyone working in this field must seek solutions by applying the basic sciences of engineering and economics in an integrated, multidisciplinary fashion (Gullichsen and Paulapuro 2000).

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