DOKUZ EYLÜL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

HEALTH AND SAFETY CONSIDERATIONS IN PRINTING

by
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March**, 2008**
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HEALTH AND SAFETY CONSIDERATION IN PRINTING

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by
Aylin ÖZMAN

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HEALTH AND SAFETY CONSIDERATIONS IN PRINTING

ABSTRACT

Nowadays industries that use chemical substances are developing. Besides the existing chemicals, many new chemical substances are produced, used, stored and transported every year. So a lot of hazardous and toxic substances are released to the environment and cause to risk for human health and the environment.

There are many factors affected employees health negatively in work environment. Some of them are unhealthy working medium, physical and chemical factors. Employers should provide good working medium to the employees. Anyhow occupational health and safety is provided with laws and and regulations. But because of lack of audits, uninterest of employers, laws can’t be in force.

Many industries use chemicals and printing industry is one of them. Many chemicals such as inks, ink tiners, lacquers, lacquer-tiners, adhesives and cleaning agents used in the printing industry are hazardous to health and cause harm if they are inhaled or absorbed through the skin. Many also cause dermatitis, vertigo, lethargy and nausea or damage to the eyes. Exposure can have an immediate or long term effect. Repeated exposure to certain substances may cause damage to the lungs, liver or the central nervous system. These effects are more pronounced for lower boiling-point organic solvents.

Nowadays printers are in a state of transition from conventional methods to advanced methods. Especially UV curing technic and UV cationic inks and lacquers are studied.

In this study occupational health and safety subjects are given. Present chemicals that are in use in printing and recommended chemicals that are less harmful for the health and the environment are compared by migration tests used for packaging which is prolongation of the printing indusrty. Recommendations are given to protect workers health in printing sector. Especially chemical factors affected employees health badly in printing house are studied. Subject searched from generally Turkey, USA and EU perspectives. Subject of the thesis was also supported with already maden studies.

Keywords : Printing, ink, UV–curing, cationic, health, safety, hazardous chemicals, migration

BASKI SANAYİİNDE SAĞLIK VE GÜVENLİK

ÖZ

Endüstrileşme ile birlikte kimyasal maddeleri kullanan endüstrilerde gelişmektedir. Mevcut kimyasalların yanı sıra birçok yeni kimyasal madde üretilmekte, kullanılmakta depolanmakta ve taşınmaktadır. Böylece çok sayıda tehlikeli ve toksik madde çevreye yayılmakta ve insan ve çevre sağlığı için risk oluşturmaktadır.

Çalışma ortamında işçi sağlığını negatif olarak etkileyen birçok faktör vardır. Bunlardan bazıları sağlıksız ortam, fiziksel ve kimyasal faktörlerdir. İşverenler işçilere iyi çalışma ortamları sağlamakla yükümlüdürler. İşçi sağlığı ve güvenliği kanun ve yönetmeliklerle sağlanır, ancak otorite eksikliği, işverenin ilgisizliği yüzünden kanunlar yeterince uygulanamamaktadır.

Birçok endüstri, kimyasalları kullanır ve baskı sanayi de bunlardan biridir. Baskı sanayiinde kullanılan birçok kimyasal (mürekepler, tinerler, laklar, yapıştırıcılar ve temizlik maddeleri) insan sağlığı açısından zararlıdır ve solunduğunda ya da deri yoluyla alındığında tehlike yaratır. Bu kimyasallardan bazıları dermatit hastalığına (deri iltihabı), baş dönmesi, uyuşukluk bulantı gibi şikayetlere yol açar veya gözlere zarar verir. Bu kimyasallara maruz kalmak hemen etkisini gösterebilir veya bu etkiler uzun vadede ortaya çıkabilir. Tekrarlayan maruz kalmalar ise akciğerlere, karaciğere, böbreklere veya merkezi sinir sistemine zarar verebilir. Bu etkiler özellikle düşük kaynama noktasına sahip organik solventler kullanıldığında daha çok ortaya çıkmaktadır.

Günümüzde matbaacılar geleneksel metotlardan modern metotlara geçiş halindedir. Özellikle UV baskı tekniği hatta UV katyonik mürekkep ve laklar üzerinde çalışılmaktadır. Türkiye’de her ay tahminen 60-85 ton UV-lak, 20-30 ton yardımcı maddeler ve 40-60 ton da temizlik solventi kullanılır. Bu rakamlar problemin içeriğini göstermektedir.

Bu çalışmada matbaada iş sağlığı ve güvenliği konusu verilmiştir. Baskıda kullanılan mevcut kimyasallar ve çevre ve insan sağlığı açısından daha az tehlikeli olan, önerilen kimyasallar baskının devamı olan ambalajlamada kullanılan migrasyon testleriyle karşılaştırılmıştır. Baskı sanayiinde işçi sağlığını korumak için öneriler verilmiştir. Konu Avrupa Birliği, Amerika ve Türkiye açısından araştırılmıştır. Konu daha önce yapılan çalışmalarla da desteklenmiştir.

Anahtar sözcükler: Baskı, mürekkep, UV kürleme, katyonik, sağlık, güvenlik, tehlikeli kimyasallar, migrasyon

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CHAPTER ONE

INTRODUCTION

1.1 What is Hazardous Chemical?

Hazardous chemicals are the chemicals that have some effects to health and environment or cause fire and explosion hazards (http://chemcareasia.wordpress.com/?s=inhalation, 2007).

-A health risk; toxic or very toxic, corrosive, harmful, irritant, sensitizing, cancer causing, effect to the reproduction systems
-Fire and explosion hazards; explosive, oxidizing, flammable
-Dangerous for the environment; toxic to living organisms, persistence in the environment, bioaccumulation

Many specific chemicals in widespread use are hazardous for living organisms, materials, structures, or the environment because of their chemical reactivities, fire hazards, corrosivities, toxicities, and other characteristics (Vatansever, 2002).

Negative impacts of chemicals are showed in Figure 1.1 as you can see from this figure chemical can cause accidents despite the good properties (Özcan, 2001).

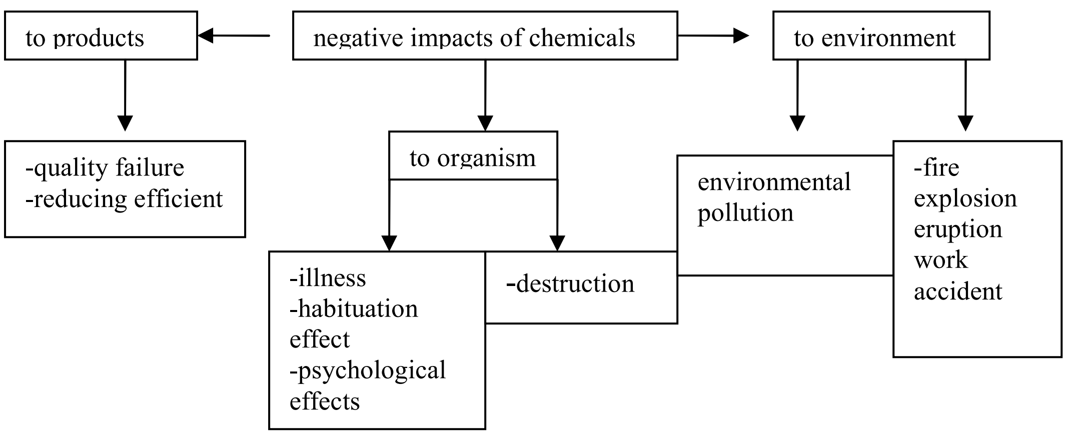


Figure 1.1 Negative impacts of chemicals (Özcan, 2001)

On the other hand OSHA gives different definition; hazardous chemical means a chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term "health hazard" includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes.
(http://www.research.northwestern.edu/research/ORS/hazcomm/hazcomm-3.htm)

Hazardous and toxic substances are defined as those chemicals present in the workplace which are capable of causing harm. In this definition, the term chemicals includes dusts, mixtures, and common materials such as paints, fuels, and solvents. OSHA currently regulates exposure to approximately 400 substances. The OSHA Chemical Sampling Information file contains listings for approximately 1500 substances; the Environmental Protection Agency's (EPA) Toxic Substance Control Act (TSCA) Chemical Substances Inventory lists information on more than 62,000 chemicals or chemical substances; some libraries maintain files of material safety data sheets (MSDS) for more than 100,000 substances (http://www.osha.gov/SLTC/hazardoustoxicsubstances, 2006).

Another definition is here from Yang Hu & Raymond, (2004) hazardous substance includes, but is not limited to, any element, substance, compound, or mixture, including disease-causing agents, which after release into the environment and upon exposure, ingestion, inhalation, or assimilation into any organism, either directly from the environment or indirectly by ingestion through the food chain, will or may reasonably be anticipated to cause death, disease, behavioral abnormalities, cancer, genetic mutation, physiological malfunctions (including malfunctions in reproduction) or physical deformations, in such organisms or their offspring. (Yang Hu & Raymond, 2004).

In Turkey at the end of the study of chemicals inventory and priority settingş in Technical Assistance Project in the field of Chemicals TeAch project a first overview of 1,400 chemicals in the Turkish market; preliminary priority chemicals list of approximately 100 different priority chemicals has been prepared for Turkey based on the results of the first survey (Ministry of Environment and Forestry, 2007).

1.1.1 Chemicals In the Environment/Waste

Chemicals have become a part of our life, sustaining many of our activities, preventing and controlling diseases, and increasing agricultural productivity. However, one can not ignore that these chemicals may, especially if not properly used, endanger our health and poison our environment (http://chemcareasia.wordpress.com/?s=inhalation, 2007).

An estimation of one thousand new chemicals enter the market every year, and about 100000 chemical substances are used on a global scale. These chemicals are mostly found as mixtures in commercial products. One to two million such products or trade names are available.

More substances and rising production mean more storage, transport, handling, use and disposal of chemicals. The whole lifecycle of a chemical should be considered when assessing its dangers and benefits.

Most chemical accidents have a limited effect. Occasionally there is a disaster like the one in Bhopal, India, in 1984, with thousands of deaths and many people permanently disabled.

Not only the worker handling chemicals is at risk. We may be exposed to chemical risks in our homes through misuse or by accidents. The environment may be affected, chemicals may pollute the air we breathe, the water we drink, and the food we eat. They may have entered into forests and lakes, destroying wildlife and changing the ecosystem.

Chemicals react in the same characteristic ways whether they are wastes or are used in a production process. The hazards are also the same.

The environment has a certain capacity to biodegrade toxic substances. However, some substances are resistant to decomposing processes. The adverse effects increase with the concentration of these substances and their accumulation in food chains.

In the natural environment, large numbers of potentially toxic substances are present. In some cases, when the substance is on its own it would cause no harm but it may interact with other toxic substances or under specific conditions it may be concentrated or transformed to a more dangerous compound. An example of an air pollution reaction is the production of photochemical smog in large cities.

Chemicals may add the adverse effects: chlorinated hydrocarbons such as DDT and dieldrin have similar chemical and biological effects. When present together they lead to more serious effects than when acting separately.

Where chemicals are used, the enterprise should plan the whole life cycle of the chemical, also the disposal of the chemical. The planning should include labelling, collecting and handling of wastes. Some countries have introduced legislation and provide detailed advice on how to treat dangerous chemical waste.

From the shop-floor, where the chemicals are actually used, up to the management, which should plan the whole, safe `lifecycle' for every substance, as well as cooperation with and within authorities is needed to use chemicals to benefit and to minimize the hazards from the use (http://chemcareasia.wordpress.com/?s=inhalation, 2007).

1.2 Types of Hazardous Substances

The management of hazards posed by hazardous substances is a crucial part of the operation of any modern chemicals industry, and a significant and increasing part of the cost of any business dealing with chemical products and processes. Personel working with such products and processes must have a good understanding of hazardous substances (Vatansever, 2002).

It is vitally important that concise guidelines be expressed in clear and understandable terms, so as to provide essential information not only on the risk potential of the substance, but above all on the measures to minimize such risks. These ideas are implemented in practice via the danger classification in conjunction with the danger guidelines and information on reducing risk, generally using one or more danger symbols accompanied by standard wording describing, very clearly and in terms comprehensible to all, the risk associated with a possible use of the chemical substance, and the measures to be adopted to prevent exposure and reduce the consequences of accidents(Vatansever, 2002)

Such classification systems generally tend to cover all possible effects of a substance, and are intended to inform users directly through the labelling. More specialized types of classification exist, aimed at specific end points, such as carcinogenesis; these classifications are drawn up by national and international agencies (Environmental Protection Agency-EPA, The International Agency for Research on Cancer –IARC, etc.) and are regularly updated, with the aim of protecting human health, particularly that of exposed workers.

Besides these “specific” classifications, there are more widely used “generic” classifications. The two systems that are most widely used are (Vatansever, 2002):

1. The United Nations (UN) classification system for the transport of dangerous goods,
2. The European Union (EU) classification system for the introduction of dangerous substances on to the market.

There are numerous kinds of hazardous substances, usually consisting of mixtures of specific chemicals.

If we consider some of the major classes of hazardous materials according to the criteria of the United States Department of Transportation (DOT); one of the most obvious of these consists of explosives. Examples include Class A explosives, such as dynamite or black powder, that are sensitive to heat and shock; Class B explosives, such as rocket propellant powders, in which contaminants may cause explosion; and Class C explosives, such as ammunition, which are subject to thermal or mechanical detonation. Compressed gases and special forms of gases may be hazardous. Examples of the former include hydrogen and sulfur dioxide, whereas acetylene gas in acetone solution is an example of the latter(Vatansever, 2002).

DOT recognizes a wide range of flammable liquids, such as gasoline and aluminum alkyls, as hazardous materials.

Flammable solids are those that burn readily, are water-reactive, or spontaneously combustible; examples include substances such as magnesium metal, sodium hydride, and calcium carbide.

Oxidizing materials include oxidizers (for example, lithium peroxide, etc.) that supply oxygen for the combustion of normally nonflammable materials.

Corrosive materials may cause disintegration of metal containers or flesh, examples of these are oleum, sulfuric acid and caustic soda.

Poisonous materials include Class A poisons, such as hydrocyanic acid, which are toxic by inhalation, ingestion, or absorption through the skin; Class B poisons, such as aniline; and etiologic agents, including causative agents of anthrax, botulism, or tetanus. Radioactive materials include plutonium, cobalt-60, and uranium hexafluoride.

On the other hand, under the authority of the Resource Conservation and Recovery Act (RCRA), the United States Environmental Protection Agency (EPA) defines hazardous substances in terms of the characteristics of ignitability, corrosivity, reactivity, and toxicity. These are explained below (Manahan, 1989):

The substances classified as ignitable are liquids whose vapors are likely to ignite in the presence of ignition sources, non-liquids that may catch fire from friction or contact with water and which burn vigorously or persistently, ignitable compressed gases, and oxidizers.

A *flammable* substance is something that will burn readily, whereas a *combustible* substance requires relatively more persuasion to burn. Maybe most chemicals that are likely to burn accidentally are liquids. Liquids form vapors that are usually denser than air, and thus tend to settle. The tendency of a liquid to ignite is measured by a test in which the liquid as heated and periodically exposed to a flame until the mixture of vapor and air ignites at the liquid's surface. So, the temperature at which this occurs is called the flash point.

It is possible to divide ignitable materials into four major classes. A flammable solid is one that can ignite from friction or from heat remaining from its manufacture, or which may cause a serious hazard if ignited. Explosive materials are not included in this classification. A flammable liquid is one having a flash point below 37.8^{o}C. Also a combustible liquid has a flash point in excess of 37.8^{o}C, but below 93.3^{o}C. Gases are substances that exist entirely in the gaseous phase at 0^{o}C and 1 atm pressure. So, a flammable compressed gas meets specified criteria for lower flammability limit, flammability range, and flame projection. Two important concepts are flammability limit and flammability range in considering the ignition of vapors. Values of the vapor/air ratio, below which ignition cannot occur because of insufficient fuel, define the lower flammability limit. Similarly, values of the vapor/air ratio, above which ignition cannot occur because of insufficient air, define the upper flammability limit. The temperature is the flammability range. For best combustion (most explosive mixture), the percentage of flammable substance is labelled "optimal". One of the more disastrous problems that can occur with flammable liquids is a boiling liquid expanding vapor explosion. This is caused by rapid pressure build up in closed containers of flammable liquids heated by an external source. The explosion occurs when the pressure build up is sufficient to break the container walls. Finely divided particles of combustible materials are analogous to vapors in respect to flammability. Dust explosions can occur with a large variety of solids that have been ground to a finely divided state. For example many metal dusts, particularly those of magnesium and its alloys, zirconium, titanium, and aluminum can burn explosively in air. In addition, coal dust and grain dusts have caused many fatal fires and explosions in coal mines and grain elevators, respectively. Dusts of polymers such as cellulose acetate, polyethylene, and polystyrene can also be explosive. Combustible substances are reducing agents that react with *oxidizers* (oxidizing agents or oxidants) to produce heat. Diatomic oxygen, O_2, from air is the most common oxidizer.

Besides this, many oxidizers are chemical compounds that contain oxygen in their formulas. The halogens (periodic table group 7A) and many of their compounds are oxidizers. The toxic effects of some oxidizers are due to their ability to oxidize bio-molecules in living systems. Whether or not a substance acts as an oxidizer depends on the reducing strength of the material that it contacts. So, oxidizers can contribute strongly to fire hazards because fuels may burn explosively in contact with an oxidizer.

Substances that catch fire spontaneously in air without an ignition source are called *pyrophoric*. These include several elements such as white phosphorus, the alkali metals (group 1A), and powdered forms of magnesium, calcium, cobalt, manganese, iron, zirconium and aluminum.

Many mixtures of oxidizers and oxidizable chemicals catch fire spontaneously. They are called *hyperbolic mixtures*. For example, nitric acid and phenol form such a mixture.

Some of the greater dangers of fires are from toxic products and byproducts of combustion. The most obvious of these are toxic CO, SO_2, P_4O_{10}, HCl, and aldehydes. In addition to forming carbon monoxide, combustion under oxygen deficient conditions produces polycyclic aromatic hydrocarbons consisting of fused ring structures, such as benzo(a)pyrene, are precarcinogens.

Corrosive substances may exhibit extremes of acidity or basicity or a tendency to corrode steel. They are regarded as those that dissolve metals or cause oxidized material to form on the surface of metals, such as rusted iron. Corrosives cause deterioration of materials, including living tissues that they contact. Most corrosives belong to at least one of the four following chemical classes: strong acids, strong bases, oxidants, dehydrating agents. Sulfuric acid is a main example of corrosive substances. As well as being a strong acid, concentrated sulfuric acid is also an oxidant and dehydrating agent. Some dehydration reactions of sulfuric acid can be very vigorous. For example, the reaction with perchloric acid produces unstable Cl_2O_7, and a violent explosion can result. Concentrated sulfuric acid produces dangerous or toxic products with a number of other substances, such as toxic carbon monoxide (CO) from reaction with oxalic acid, $H_2C_2O_4$; toxic bromine and sulfur dioxide (Br_2, SO_2) from reaction with sodium bromide, NaBr; and toxic, unstable chlorine dioxide (ClO_2) from reaction with sodium chlorate, $NaClO_3$.

Reactive substances are those with a tendency to undergo rapid or violent chemical change under certain conditions. Such substances include those that react violently or form potentially explosive mixtures with water; an explosive substance is an obvious example. Explosives constitute another class of reactive substances. Substances are also classified as reactive that react with water, acid, or base to produce toxic fumes, particularly those of hydrogen sulfide or hydrogen cyanide. Some chemical compounds are self-reactive, in that they contain oxidant and reductant in the same compound. For example trinitrotoluene, TNT is an explosive with a high degree of reactivity. However, it is inherently relatively stable in that some sort of detonating device is required to cause it to explode. In dealing with hazardous substances, toxicity is of the utmost concern. It includes both long-term chronic effects from continual or periodic exposures to low levels of toxicants and acute effects from a single large exposure.

The characteristic of toxicity is defined in terms of a standard extraction procedure followed by chemical analysis for specific substances. For regulatory and remediation purposes, a standard test is needed to measure the probability of toxic substances getting into the environment and causing harm to organisms.

Besides these, according to the Council Directive 91/689/EEC of 12 December 1991 on Hazardous Wastes In European Community, properties of substances which render them hazardous are defined as follows: Explosives are substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene. Oxidizings are substances and preparations that exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances. Highly flammables are liquid substances and preparations having a flash point below 21°C (including extremely flammable liquids), or- substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any application of energy, or - solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition, or-gaseous substances and preparations which are flammable in air at normal pressure, or-substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.

Flammables are liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C are non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.

Harmfuls are substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.

Toxics are substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.

Carcinogenic substances are substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.

Corrosives are substances and preparations, which may destroy living tissue on contacts.

Infectious substances are substances containing viable microorganisms or their toxins, which are known or reliably believed to cause disease in man or other living organisms.

Teratogenic substances are substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence.

Mutagenic substances are substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.

Ecotoxic substances are substances and preparations, which present or may present immediate or delayed risks for one or more sectors of the environment.

'Irritants are non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.

In Turkey with the 6th of the November in 2001 chronogram and 24575 numbered decision in formal newspaper, “Hazardous Chemicals Regulation” was publicated. And 4th item of this regulation includes some chemical properties used in Printing and Package Industry:

1-Flammable substances 2-Highly toxic substances 3-Harmful substances 4-Corrosive substances 5-Irritative substances 6-Allergic substances 7-Carcinogenic substances 8-Mutagen substances 9-Heavy metal pigments and fillings

These properties have same definitions and properties with directive 91/689/EEC, anyhow Hazardous Chemicals Regulation is adapted with this directive.

1.3 Common Accidents Related To Hazardous Chemicals

There are three types of events traditionally associated with the chemicals industry (Vatansever, 2002):

1. Releases and spills (Seveso, Bhopal,1984)
2. Fires (Basel, 1986)
3. Explosions (Flixborough)

On July 10, 1976 the accidental release of a chemical cloud containing 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD) into the atmosphere near Seveso, Italy caused a serious environmental contamination. An estimated 200–500 g of this toxic compound was released into the environment, contaminating an area of 3 km^2 (Buser, 2001).

The Bhopal gas tragedy occurred in December 1984 where in approximately 41 tonnes of deadly MIC was released in the dead of night. It caused the death of over 3000 people and continued life-long misery for over 300,000 with certain genetic defects passed on to the next generation. It happened in a plant operated by a multinational, Union Carbide Corporation, in a developing country, India (Gupta, 2001).

Thirty tons of toxic material washed into the Rhine River with water firefighters used to fight a warehouse blaze at a riverside Sandoz chemical plant and storage facility near Basel, Switzerland in the early morning hours of November 1, 1986. By the time the chemicals, mostly pesticides, had traveled 500 miles down the winding scenic river, half a million fish were dead, several municipal water supplies were contaminated, and the Rhine's ecosystem was badly damaged with virtually all marine life and a large proportion of microorganisms wiped out (United States Fire Administration National Fire Data Center).

On 1 June 1974 an explosion occurred at the Nypro (UK) Ltd. plant at Flixborough (Lincolnshire) resulting in the death of 28 employees and injuries to others working at the plant and severe structural damage. Injuries to the public and damage to property also occurred beyond the plant boundary. Fires on the plant resulting from the explosion burned for several days. The explosion followed the ignition of a cloud of cyclohexane vapour mixed with air which was produced by the failure of one of the pipes between five inter-connected oxidation vessels containing cyclohexane at 150° C and a pressure of 1 MPa (Sadée, Samuels & O'Brien, 1977).

Damage caused by the above-mentioned types of event comes about through two distinct processes Vatansever, 2002):

1. Direct action of chemicals on humans and the environment
2. Indirect action of liberated energy

So that, the dangers arising from chemical plants have much to do with the nature of the substances being processed, the way they are treated in the plant, and their tendency to take part in chemical reactions under these conditions. Besides these, a conflict arises between process needs and chemical safety. On the one hand, chemistry requires reactive substances; on the other hand, this reactivity of the substances is a key aspect of the danger they pose. A chemical process is not possible without substances that show hazardous properties and effects. Therefore the substances must be reliably contained in the process equipment, and their reactivity must be governed so that uncontrolled chemical reactions cannot take place(Vatansever, 2002).

CHAPTER TWO
PRINTING

2.1 General Information About Printing

Printing is a process used to transfer images or material to a substrate. From the printing industries perspective the industry is organized by the type of printing process used: Lithography, Gravure, Flexography, Screen and Letterpress (EPA, 1994).

2.1.1 Lithographic Printing

A planographic printing system where the image and nonimage areas are chemically differentiated. The image area is oil receptive and nonimage area is water receptive. Ink film from the lithographic plate is transferred to an intermediary surface (blanket), which, in turn, transfers the ink film to the substrate. Fountain solution is applied to maintain the hydrophilic properties of the nonimage area. Ink drying is divided into heatset and non heatset.

Lithographic printing is showed in figure 2.1 schematically below.

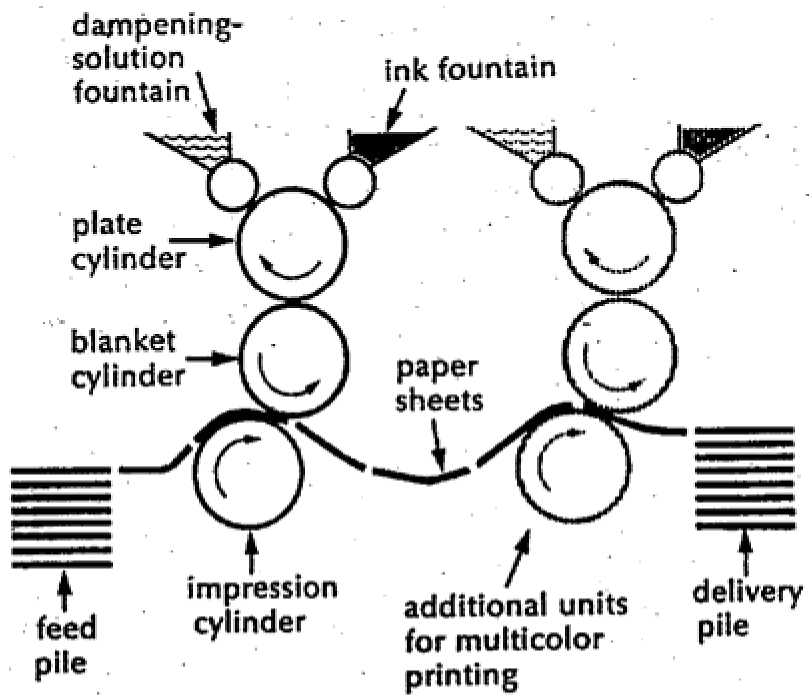


Figure 2.1 Lithographic printing (EPA, 1995)

2.1.1.1 Fountain Solution

A mixture of water and other volatile and non-volatile chemicals and additives that maintains the quality of the printing plate reduces the surface tension of the water so that it spreads easily across the printing plate surface. The fountain solution wets the nonimage area so that the ink is maintained within the image areas. Non-volatile additives include mineral salts and hydrophilic gums. Alcohol and alcohol substitutes, including isopropyl alcohol, glycol ethers, and ethylene glycol, are the most common volatile organic compounds (VOC) additives used to reduce the surface tension of the fountain solution.

2.1.1.2 Heatset

A lithographic web printing process where heat is used to evaporate ink oils from the printing ink. Heatset dryers (typically hot air) are used to deliver the heat to the printed web.

2.1.1.3 Non-Heatset

A lithographic printing process where the printing inks are set without the use of heat. Traditional non-heatset inks set and dry by absorption and/or oxidation of the ink oils. Ultraviolet-cured and electron beam-cured inks are considered non-heatset although radiant energy is required to cure these inks.

2.1.2 Flexographic Printing

A printing system using a flexible rubber or elastomeric image carrier in which the image area is raised relative to the nonimage area. The image is transferred to the substrate through first applying ink to a smooth roller which in turn rolls the ink onto the raised pattern of a rubber or elastomeric pad fastened around a second roller which then rolls the ink onto the substrate. Flexographic printing is showed in figure 2.2 schematically below.

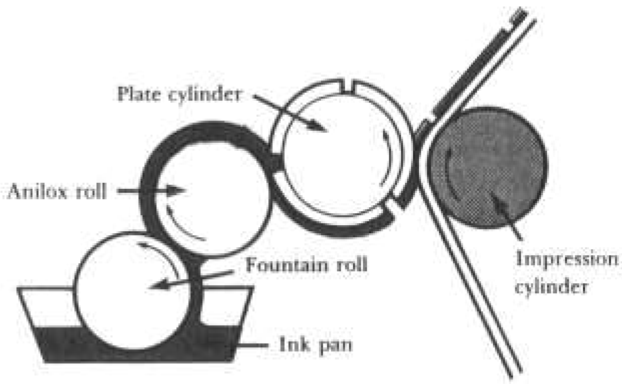


Figure 2.2 Flexographic printing (EPA, 1995)

2.1.3 Rotogravure Printing

A printing system using a chrome plated cylinder where the image area is recessed relative to the nonimage area. Images are transferred onto a substrate through first applying ink to a cylinder into the surface of which small, shallow cells have been etched forming a pattern, then wiping the lands between the cells free of ink with a doctor blade, and finally rolling the substrate over the cylinder so that the surface of the substrate is pressed into the cells, transferring the ink to the substrate. Rotogravure printing is showed in figure 2.3 schematically below.

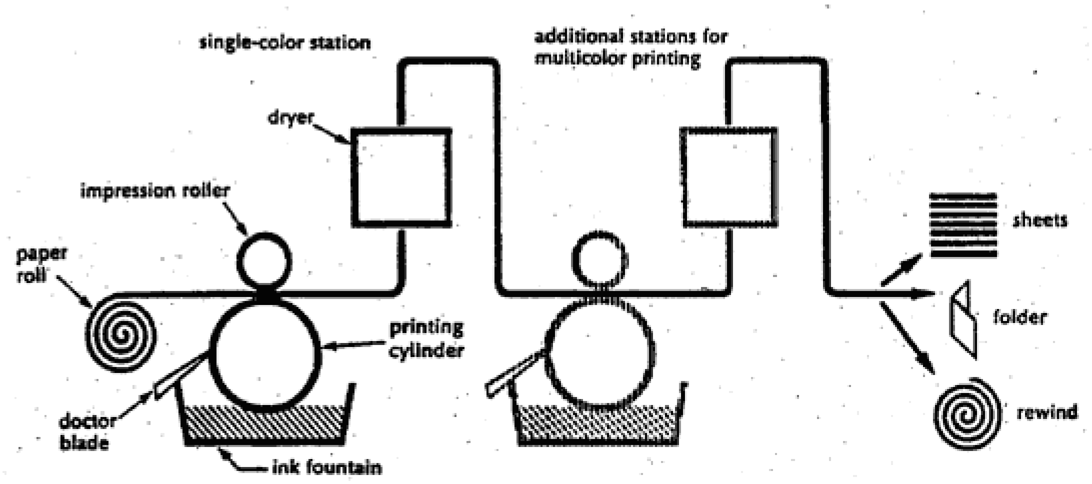


Figure 2.3 Rotogravure printing (EPA, 1995)

2.1.4 Screen Printing

A printing system where the printing ink passes through a web or fabric to which a refined form of stencil has been applied. The stencil openings determine the form and dimensions of the imprint. Screen printing is showed in figure 2.4 schematically next page.

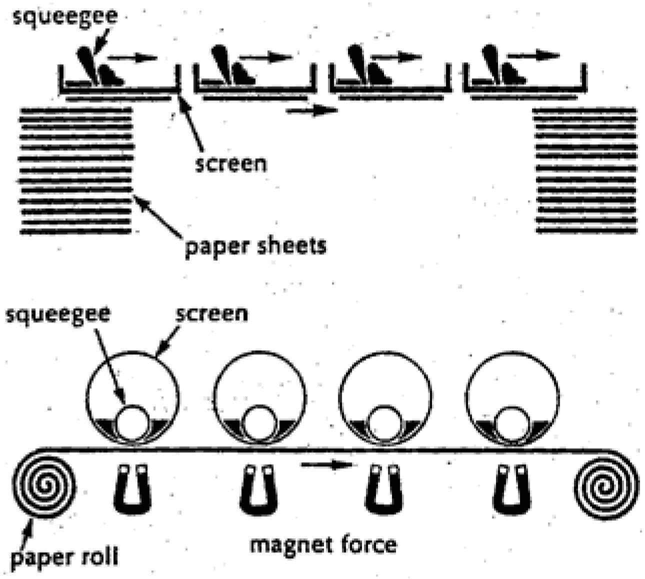


Figure 2.4 Screen printing (EPA, 1995)

2.1.5 Letterpress Printing

A printing system in which the image area is raised relative to the nonimage area and the ink is transferred to the substrate directly from the image surface. Letterpress printing is showed in figure 2.5 and 2.6 schematically below.

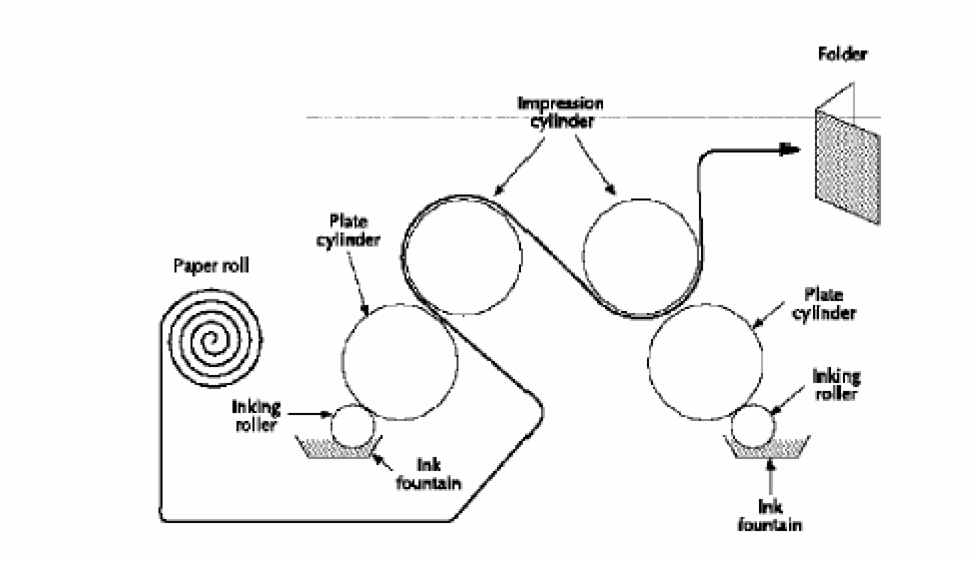


Figure 2.5 Letterpress printing (EPA, 1995)

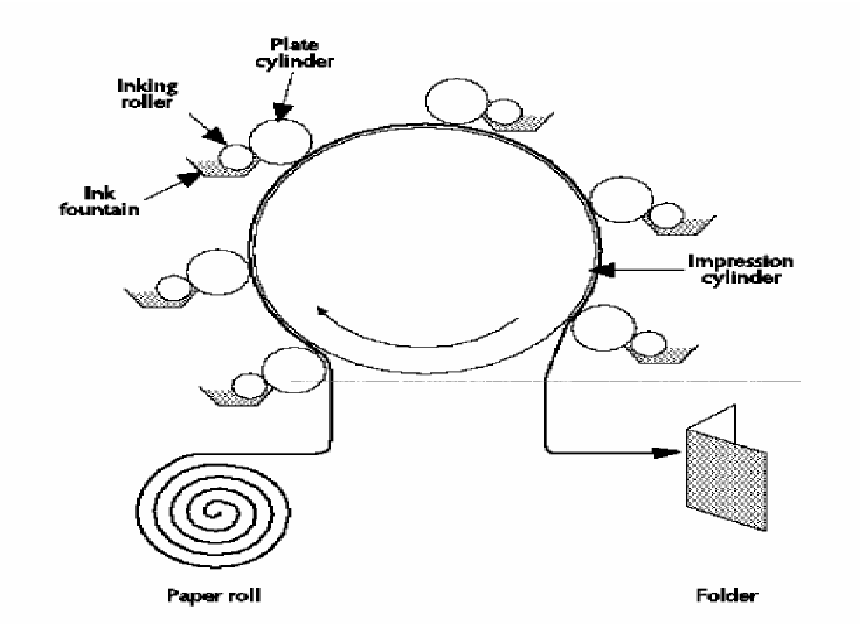


Figure 2.6 Letterpress printing (EPA, 1995)

The equipment, applications and chemicals for each of these process differ; however they all print an image on a substrate following the same basic sequence. The fundamental steps in printing are referred to as imaging, pre-press, printing and post press operations.

The type of printing technology that is used depends on a variety of factors, including the substrate used (paper, plastic, metal, ceramic, etc.), the length and speed of the print run, the required print image quality, and the end product produces (EPA, 1994).

2.2 What is Ink?

Ink is a substance that provides transferring any motif, picture, article and shape to printing materials. Its composition can change depending on the type of printing surface(United States Cencus, 1997).

2.2.1 The History of Ink Production

Writing inks were first manufactured in both ancient Egypt and China in about 2500 Before the Christian era (BC). These inks were composed of soot bound together with gums. This paste was formed into rods and dried, then mixed with water immediately before use. Printing was invented by the Chinese about 3000 years later. They used a mixture of coloured earth, soot and plant matter for pigments, again mixed with gums for a binder. By 1440, when Johannes Guttenberg invented the first printing press with moveable type, ink was made of soot bound with either linseed oil or varnish - similar materials to those used for black inks today. Coloured inks were introduced in 1772 and drying agents were first used in the nineteenth century (Wansbrough, Taylor, & Yuen, 2007).

Today's printing inks are composed of a pigment (one of which is carbon black, which is not much different from the soot used in 2500 BC), a binder (an oil, resin or varnish of some kind), a solvent and various additives such as drying and chelating agents. The exact recipe for a given ink depends on the type of surface that it will be printing on and the printing method that will be used. Inks have been designed to print on a wide range of surfaces from metals, plastics and fabrics through to papers. The various printing methods are all similar, in that the ink is applied to a plate/cylinder and this is applied to the surface to be printed (Wansbrough, Taylor, & Yuen, 2007).

However, the plate/cylinder can be made of metal or rubber, and the image can be raised up above the surface of the plate, in the plane of the plate but chemically treated to attract the ink, or etched into the plate and the excess ink scraped off. Different inks are produced to suit these different conditions.

2.2.2 Ink Systems

Ink is a substance that provides transferring any motif, picture, article and shape to printing materials. Its composition can change depending on the type of printing surface. The ink systems can be classified in three categories (U.S.Cencus, 1997):

2.2.2.1 Solvent-based Ink

These inks dry by evaporation, the solvents usually contain significant amount of VOC's (volatile organic compounds) which are usually flammable, and they contribute to the formation of ground level ozone (a component of smog), which causes respiratory and other health problems. Solvent based ink systems are equipped with oxidizers and other pollution control devices to destroy VOC's.

2.2.2.2 Water-based Inks

Although the primary solvent in these inks is water, they can and usually do contain VOC's, up to a maximum of 25% by volume. They may also contain one or more of the 188 hazardous air pollutants that were listed in the 1990 Clean Air Act. Depending on their hazardous air pollutant (HAP) and VOC content, water based inks may or may not have fewer health and environmental concern than traditional solvent based inks. Depending on their VOC content, water based inks show a range of flammability.

2.2.2.3 UV-cured Inks

These are the newest ink system in printing. The use of UV inks has been steadily increasing, especially for narrow-web labels and tags. Chemicals in UV- cured inks form solids and bond to the substrate when they are exposed to ultraviolet light, whereas solvent based and water based inks dry by evaporation. Because of this difference, UV-cure inks do not contain traditional solvents, so they may have very low VOC content. However they do contain many chemicals that have not been tested comprehensively for environmental health safety impacts.

2.2.3 Components of Printing Inks

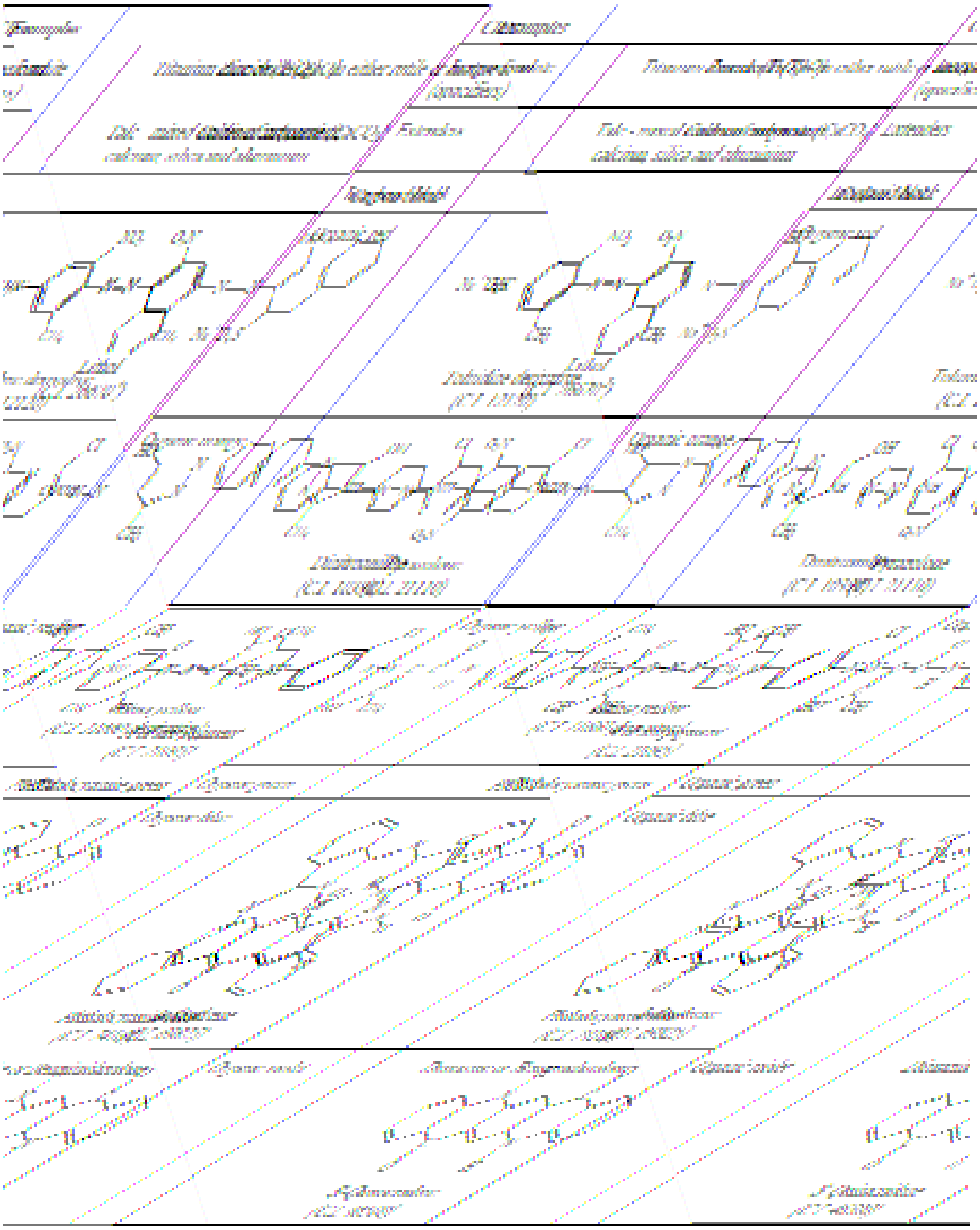
The raw materials for ink production are pigments, binders, solvents and additives. These materials are discussed below (Wansbrough, Taylor, & Yuen, 2007).

2.2.3.1 Pigments

The most obvious role of a pigment is to colour the ink. However, they can also provide gloss, abrasiveness and resistance to attack by light, heat, solvents etc.

Table 2.1 shows the common printing ink pigments next page:

Table 2.1 Common printing ink pigments



[3]Pigments are assigned a five digit number based on structure in the American Colour Index.

2.2.3.2 Binders

Resins and the oils are the binders.

Resins

Resins are primarily binders, they bind the other ingredients of the ink together so that it forms a film and they bind the ink to the paper. They also contribute to such properties as gloss and resistance to heat, chemicals and water. Many different resins are used, and typically more than one resin is used in a given ink. The most commonly used resins are listed in Table 2.2 below:

Table 2.2 The most commonly used resins

Acrylics	Ketones	Alkyds	Maleics
Cellulose derivatives	Formaldehydes	Rubber resins	Phenolics
Epoxides	Poly vinyl butyral	Fumarics	Polyamides
Hydrocarbons	Shellac	Isocyanate free polyurethanes	

Oils

They are bindings that provide brightnesss of inks and chemical resistances. The oil or carrier is the medium for transferring the pigment and resin through the press to the paper.

2.2.3.3 Solvents

Solvents are used to keep the ink liquid from when it is applied to the printing plate or cylinder until when it has been transferred to the surface to be printed. At this point the solvent must separate from the body of the ink to allow the image to dry and bind to the surface.

Some printing processes (e.g. the gravure and flexographic processes) require a solvent that evaporates rapidly. These use volatile solvents (i.e. those with boiling points below 120^0 C) such as those listed in Table 2.3.

Table 2.3 Volatile printing ink solvents

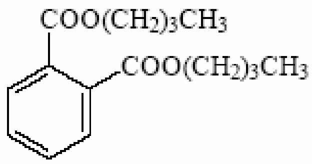
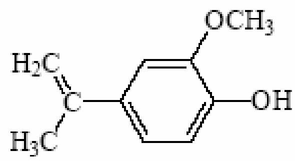
Name	Structure or composition	Boiling point / °C
methylated spirits		
ethyl acetate	$CH_3COOCH_2CH_3$	77
isopropanol	$CH_3CHOHCH_3$	82.5
n-propyl acetate	$CH_3COOCH_2CH_2CH_3$	101.6

High-boiling point (T_b = 240 - 320°C) hydrocarbons are chosen as solvents for lithographic inks as the solvent used must be viscous and hydrophobic.

2.2.3.4 Additives

Many different types of additives are used to alter the final properties of the paint. The most common types of additives (with typical examples) are listed in Table 2.4 next page:

Table 2.4 The most common types of additives

Type	**Function**	**Typical example**
Plasticiser	Enhances the flexibility of the printed film	 dibutyl phthalate
Wax	Promotes rub resistance	Carnauba - an exudate from the leaves of *Copernicia prunifera*. Consists of esters of hydroxylated unsaturated fatty acids with at least twelve carbon atoms in the acid chain.
Drier	Catalyses the oxidation reaction of inks which dry by oxidation	salts or soaps of cobalt, manganese or zirconium
Chelating agent	Increases the viscosity of the ink (aluminium chelate) and promotes adhesion (titanium chelate)	
Antioxidant	Delays the onset of oxidation polymerisation by reacting with free radicals formed during the autooxidation thus preventing them from reacting further	 eugenol
Surfactants[10]	Improves wetting of either the pigment or the substrate	
Alkali	Controls the viscosity / solubility of acrylic resins in water based inks	$HOCH_2CH_2NH_2$ monoethanolamine
Defoamer	Reduces the surface tension in water based inks, meaning that stable bubbles cannot exist	hydrocarbon emulsions

[9]Rheology is the study of how particular fluids flow.
[10]See soap article, XI-A

2.2.4 Ink Drying and Curing

After the ink has been applied to the surface to be printed it must bind there to ensure it stays. This can happen simply as a result of the ink drying, or can take place in a series of cross-linking and polymerisation reactions that form a film and to bind it to the printed surface. These reactions are known as curing reactions. Ink drying and curing can happen *via.* any one (or a combination) of the following processes (Wansbrough, Taylor, & Yuen, 2007):

•*Oxidation*. If drying oil is present in the solvent, it will react with oxygen in the atmosphere and undergo curing reactions. Oxidation is polymerization of the binders so it is chemical drying type.

•*Evaporation*. Some inks, usually those used in applications where speed is important, are designed to dry and cure as the solvent evaporates off. Volatile solvents such as methylated spirits are usually used, but solvents with boiling points above 120 ^{0}C are used for screen-printing inks to prevent the ink from drying during application.

•*Penetration*. Inks that are printing on porous surfaces are sometimes designed so that the solvent penetrates into the bulk of the printing surface, leaving dry ink on the surface. Liquid phase of the printing ink is absorbed in a high rate by the surface of the paper and being form paper-printing ink bond one part of the binder is stayed in the printing inks on surface to keep in together of pigments and this is completed in only 2 minutes. Evaporation and penetration are physical drying types (Akgün, & İmer, 2001)

•*Radiation curing*. Radiation (usually UV) is fired at the ink, instigating a series of polymerisation reactions. Inks cured with polymerization under UV light. Most of the inks that cure with this way are water-based inks. Radiation is chemical drying methods.

-*Precipitation*. Excess water (usually in the form of steam) is added to an ink system that is only sparingly miscible in water. The sudden increase in diluent concentration causes the solubility of the resin to decrease sharply and the resin precipitates onto the printed surface. The excess water evaporates off.

2.3 Relationship Between Printing Inks and Printing Types

There are five main printing processes mentioned in chapter 2.1, and inks are designed for the specific process. Lithography and letterpress are collectively known as the 'paste ink' processes and use inks that are essentially non-volatile at normal temperatures. Flexography and gravure are known as the 'liquid ink' processes and are based upon volatile solvents that evaporate readily at room temperatures. Screen printing uses inks that fall between the other two groups (International Agency for Research on Cancer, 1996).

Choice of the vehicle (solvent with resins) for a printing ink depends on the printing process, how the ink will be dried, and the substrate on which the image is to be printed. In lithography and letterpress, where inks are dried by absorption and oxidation, vehicles are generally mixtures of mineral and vegetable oils and resins. Flexographic inks, which are designed to dry quickly by evaporation, can be either water-based or based on organic solvents (such as ethanol, ethyl acetate, *n*-propanol or isopropanol) with a wide variety of resins. Vehicles for gravure inks, which also dry by evaporation, may also contain aromatic or aliphatic hydrocarbons and ketones as solvents. Inks for screen printing use organic solvents that are somewhat less volatile than those used for flexography or gravure (higher glycol ethers and aromatic and aliphatic hydrocarbons). Additives in inks include driers, waxes and plasticizers (IARC, 1996).

Ultraviolet radiation-cured inks, commonly based on acrylates, are used in all of the printing processes to varying degrees (IARC, 1996). UV curing systems will be mentioned following chapters in detail.

2.4 *Types of Chemicals Used In Printing House*

Most of chemicals used in printing house are toxic, carcinogen and addictive and also after chemical income to body they can mutate to various carcinogen and toxic component with metabolic reactions(Yiğiter, 2006).

Chemical substances are used in manufacturing ink and paper pulp, and block preparations and threats to workers health (Yiğiter, 2006).

These are: Metals-acids and bases materials-solvents-powder chemicals-organic and inorganic chemicals-pharmaceuticals, alcohols, nicotines

Metals; lead, aluminium, copper, zinc
Acid and bases; hydrochloric acids, nitric acids, sulphuric acids, acetic acids
Solvents*:* toluene, xylene
Alcohol*:* n-butanols, ethylene glyhcols, isoprophyl alcohols
Acetone and gasolines
Powder chemicals: During the ascending from paper cutting; harvesting, binding, powder, flying ink particles from web-offset machines

Other organic and inorganic chemicals*:* Different pigments, dyestuffs, lutes (filling agents) calcium sulphate, polyvinyl alcohol, starch, casein, sodium stereat and potassium stearets. Most of these chemicals are carcinogen.

The chemicals used in each ink system are given in Table 2.5

Table 2.5 Chemical categories by ink function. (U.S.Cencus, 1997):

Solvents	Colorants	Resins	Additives	Curing Compounds	Multiple Functions
Solvent based system					
Alcohols Alkyl Acetates Propylene Glycol Ethers	Organic, inorganic, and organometallic pigments	Polyol derivatives Resins	High molecular-weight HC's, Organic acids or salts Olefin polymers (waxes) Organolitanium compounds Siloxanes (defoamers and wetting agents)	none	Amides or nitrogeneous compounds (slip additives, buffers, inhibitors) Inorganics Low-molecular-weight HC's
Water based system					
Alcohols Ethylene glycol ethers Propylene glycol ethers	Organic, inorganic, and organometallic pigments	Resins	Acrylic acid polymers High-molecular-weight hydrocarbons Organic acids or salts Siloxanes (defoamers and wetting agents)	None	Amides or nitrogenous compounds (slip additives, buffers, inhibitors) Inorganics Low-molecular weight HC's
UV cured system					
Alcohols	Organic, inorganic,and organometallic pigments	Polyol derivatives Resins	Aromatic esters (plasticizers) Olefin polymers (waxes) Siloxanes (defoamers and wetting agents)	Acrylated polyols Acrylated polymers Aromatic esters Aromatic ketones Organoph. compd's	Amides or nitrogenous compounds (slip additives, buffers, inhibitors)

2.4.1 Hazardous Chemicals in Printing Industry

Many chemicals are used in printing industry. Inks, ink tiners, lacquers, lacquer-tiners, adhesives and cleaning chemicals include many types of chemicals and some of them are hazardous.

There are many studies about avoiding these chemicals usage with legislations and voluntary recommendations. Below it is mentioned about these voluntary recommendations:

For some years a number of National Association members of the European Council of Paint, Printing Ink and Artist Colours Industry (CEPE), (2001) have been independently operating voluntary recommendations for the exclusion of certain raw materials (substances and preparations according to the definition given in the Dangerous Substances Directive (67/548/EEC)) from printing inks and related products. These exclusion lists of materials have been based on health and safety matters in the day-to-day production and marketing of printing inks and associated products employing Good Manufacturing Practices.

The following categories are excluded from raw materials for the manufacture of printing inks and related products supplied to printers:

Selection Criteria: Substance or preparations previously used or relevant in the formulation of printing inks that must be avoided in consideration of the selection criteria would cause a risk to health.

A-Carcinogenic, mutagenic, and toxic for reproduction substances and preparations classified and labelled as toxic (T) according to the 67/548/EEC with risk phases R45, R46, R49, R60, R61 (the list of R- phases is in Annex III to the 67/548/EEC).

Note: With the exception of non-bioavilable pigments in which antimonyis a constituent of the crystal lattice and of organic derivatives not classified or labelled as T or T+

B-Substances and preparations classified and labelled as very toxic (T+) or toxic (T) according to the 67/548/EEC with risk phases R23, R24, R25, R26, R27, R28, R29, R48

C-Pigment colourant based on and compounds of antimony, arsenic, cadmium, chromium(VI)* , lead*, mercury, selenium.

Substances list:

D- Dye colourants:

Auramine (basic yellow2 -CI 41000)
Chrysoidine(basic orange2 -CI 11270)
Fuchsine (basic violet14 -CI 42510)
Induline (solventblue7 -CI 50400)
Cresylene Brown(basic brown4) -CI 21010)

Other soluble azo dyes which can decompose in the body to bioavilable carcinogenic aromatic amines of category 1 and 2 according to 67/548/EEC.

E-Solvents

2-Methoxyethanol
2-Ethoxyethanol
2-Methoxyethylacetate
2-Ethoxyethylacetate
monochlorobenzene
Dichlorobenzene
Volatile fluuorochlorinate hydrocarbons, such as trichloroethylene, perchloroethylene and methylene chloride

*:with the exceptions of lead pigments used for certain screen and decor inks where specific resistance *properties are needed.*

Volatile fluorochlorinated hydrocarbons
2-Nitropropane
Methanol

F-Plasticisers:

Chlorinated napthalenes
Chlorinated parafins
Monocresyl phosphate
Tricresyl phosphate
Monocresyl diphenyl phosphate

G-Various compounds:

Diaminostilbene and derivatives
2,4 –Dimethyl-6-tertiary- butylphenol
4,4 Tetramethyldiaminobenzophenone (Michler's Ketone)
Hexachlorocyclohexan

H-which are not permitted according to directive 76/769/EEC (relating to the restriction of the marketing and use of certain dangerous substances and preparations) and its amendments, such as

Asbestos
Benzene
Pentachlorophenol and its salts
PCB
PCT
VCM

I-which are not commercially available or not suitable for the formulation of printing inks and related materials such as:

Brominated flameretardants
Dioxines
Nitrosamines

Polybrominated bi-or terphenyls

Polychlorinated dibenzofuranes

The CEPE exclusion list will be under frequent review by the European Technical Commitee Printing Inks) and may be amended where appropriate, in the light of new data on safety, health and environmental matters.

2.4.2 Hazardous Chemicals In Printing, Their Health and Environmental Effects

In printing, many chemicals are used in inks, additives, cleaning products, etc. Solvents have VOC's (volatile organic compounds) which has hazardous characteristics, so they pose a serious risk for human and environmental health and safety. Some chemicals used in printing are in 'Highly Hazardous Chemical, Toxic and Reactive' List. These are; acetaldehyde, ammonia, ethylamine, formaldehyde and hydrogen chloride (Washington Industrial Safety and Health Act Services, - WISHA, 2007).

Furthermore some other chemicals used in printing are in 'Priority Pollutants' list published by Environmental Protection Agency (EPA). Priority pollutants used in printing are given in Table 2.4.

Table 2.4 Chemical which are Present in Priority Pollutants List and used in Printing Industry (US EPA, 2005).

benzene	di-n-butyl phthalate	trichloroetylene	Silver
chlorobenzene	1,1,1 trichloroethane	cadmium compounds	ethylbenzene
methylene chloride	tetrachloroetylene	chromium compounds	
izophorone	toluene	copper compounds	

During the manufacture of printing inks, exposure to pigments, vehicles and additives can occur through inhalation or skin contact during mixing and dispersion and during clean-up of mixers. Exposures are higher with liquid inks than with paste inks. During newspaper printing by letterpress or lithography, the major exposure is to ink mist. Rotary letterpress was the dominant process for the production of newspapers until the 1970s. It has now been largely replaced by web offset litho, in which exposures to ink mist are considerably lower than for letterpress. In other lithographic and letterpress printing, the major exposure is to hydrocarbon-based cleaning solvents and isopropanol from damping solutions. In flexographic, gravure and screen printing, exposures are mainly to organic solvents. Historically, some workers in both ink manufacture and printing were exposed to much higher levels of lead, polycyclic aromatic hydrocarbons and benzene than today, and the development and use of modern control technologies have made possible the marked reduction (IARC, 1996).

Some properties of chemicals used in printing industry below (EPA, 1995):

Toluene

Physical Properties. Toluene is a volatile organic chemical.

Environmental Fate. The majority of releases of toluene to land and water will evaporate. Toluene may also be degraded by microorganisms. Once volatilized, toluene in the lower atmosphere will react with other atmospheric components contributing to the formation of ground-level ozone and other air pollutants.

Toxicity. Inhalation or ingestion of toluene can cause head aches, confusion, weakness, and memory loss. Toluene may also affect the way the kidneys and liver function. Reactions of toluene (see environmental fate) in the atmosphere contribute to the formation of ozone in the lower atmosphere. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma orallergy sufferers.

Some studies have shown that unborn animals were harmed when highlevels of toluene were inhaled by their mothers, although the same effectswere not seen when the mothers were fed large quantities of toluene. Note that these results may reflect similar difficulties in humans.

Carcinogenicity. There is currently no evidence to suggest that this chemical is carcinogenic.

Glycol Ethers

Data on ethylene glycol mono-n-butyl ether (2-butoxyethanol) are used to represent all glycol ethers because it is the most commonly used glycol ether in printing.

Ethylene Glycol Mono-n-Butyl Ether (2-Butoxyethanol)

*Environmental fate***.** The chemical 2-butoxyethanol is highly mobile in soils and should not accumulate in organic matter contained in sediments and suspended solids. Limited monitoring data has shown that it can leach to ground water. Hydrolysis, direct photolysis, volatilization, adsorption, and bioconcentration are not important fate processes for 2-butoxyethanol. Biodegradation is likely to be the most important removal mechanism of 2- butoxyethanol from aerobic soil and water. In the atmosphere, it reacts with photochemically produced hydroxyl radicals with an estimated half-life of 17 hours.

Toxicity. Exposure to moderate concentrations of 2-butoxyethanol may cause central nervous system depression, including headaches, drowsiness, weakness, slurred speech, stuttering, staggering, tremors, blurred vision, and personality changes. These symptoms are such that a patient, in the absence of an accurate occupational history, may be treated for schizophrenia or narcolepsy. Other symptoms of moderate poisoning include nausea; vomiting; diarrhea; blood toxicity; abdominal and lumbar pain; and lesions in the brain, lung, liver, meninges and heart. Exposure to higher concentrations may lead to skin, respiratory, and eye irritation; kidney and liver damage; and coma.

It appears that 2-butoxyethanol is one of the few materials to which humans are more resistant than experimental animals. This appears to be at least partly due to the fact that humans are more resistant to the chemical's red blood cell-destroying properties than are most lab animals.

Methyl Ethyl Ketone

*Environmental Fate***.** MEK is a flammable liquid. Most of the MEK released to the environment will end up in the atmosphere. MEK can contribute to the formation of air pollutants in the lower atmosphere. It can be degraded by microorganisms living in water and soil.

Toxicity. Breathing moderate amounts of methyl ethyl ketone (MEK) for short periods of time can cause adverse effects on the nervous system ranging from headaches, dizziness, nausea, and numbness in the fingers and toes to unconsciousness. Its vapors are irritating to the skin, eyes, nose, and throat and can damage the eyes. Repeated exposure to moderate to high amounts may cause liver and kidney effects.

1,1,1-Trichloroethane

*Environmental Fate***.** Releases of TCE to surface water or land will almost entirely volatilize. Releases to air may be transported long distances and may partially return to earth in rain. In the lower atmosphere, TCE degrades very slowly by photooxidation and slowly diffuses to the upper atmosphere where photodegradation is rapid. Any TCE that does not evaporate from soils leaches to groundwater. Degradation in soils and water is slow. TCE does not hydrolyze in water, nor does it significantly bioconcentrate in aquatic organisms.

Toxicity. Repeated contact of 1,1,1-trichloroethane (TCE) with skin may cause serious skin cracking and infection. Vapors cause a slight smarting of the eyes or respiratory system if present in high concentrations. Exposure to high concentrations of TCE causes reversible mild liver and kidney dysfunction, central nervous system depression, gait disturbances, stupor, coma, respiratory depression, and even death.

Exposure to lower concentrations of TCE leads to light-headedness, throat irritation, headache, disequilibrium, impaired coordination, drowsiness, convulsions and mild changes in perception.

Carcinogenicity There is currently no evidence to suggest that thi chemical is carcinogenic.

Xylene (Mixed Isomers)

Environmental Fate. The majority of releases to land and water will quickly evaporate, although some degradation by microorganisms will occur. Xylenes are moderately mobile in soils and may leach into groundwater, where they may persist for several years. Xylenes are volatile organic chemicals. As such, xylenes in the lower atmosphere will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants (EPA, 1995).

It may also deal with chemicals hazards in different ways; for example, contrast the difference between the hazards of 1000 ml of Xylene (a hazardous substance) will have a hazard of harmful vapours in use, and than, say, 10,000 l of Xylene (a Dangerous Goods), which has a hazard of flammability in storage (Winder, Azzi, &Wagner, 2005).

*Toxicity***.** Xylenes are rapidly absorbed into the body after inhalation, ingestion, or skin contact. Short-term exposure of humans to high levels of xylenes can cause irritation of the skin, eyes, nose, and throat, difficulty in breathing, impaired lung function, impaired memory, and possible changes in the liver and kidneys. Both short- and long-term exposure to high concentrations can cause effects such as headaches, dizziness, confusion, and lack of muscle coordination. Reactions of xylenes (see environmental fate) in the atmosphere contribute to the formation of ozone in the lower atmosphere. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers(EPA, 1995).

Carcinogenicity. There is currently no evidence to suggest that this chemical is carcinogenic.

2.5 Printing Industry in Turkey

In Turkey, according to data obtained from Union of Chambers and Commodity of Exchanges (TOBB) Industry Database Table 2.6 is formed (Yılmaz, 2006).

According to information obtained via personal communication weight of the newspaper changes within the range of 48.8 – 52 g/m^2 with an average of 50 g/m^2. This means that each year the amount of newspaper printed is 445,450 tons. Other than that information about the weight of books, magazines, brochure lacks. It is difficult to estimate the total weight of material printed as books, magazines, brochures etc. These items can be printed on glossy paper, first grade paper or second grade paper. It is assumed that the weight of these paper are around 60 g/m^2 which leads to total amount of 16,244 tons of paper printed as book, magazines and brochure (Yılmaz, 2006).

Table 2.6 Capacity of printing industry in Turkey (Yılmaz, 2006)

Printing type	Printing process	Capacity
Newspaper printing	Offset lithography or relief printing	650,029,464 pieces
		8,909,032,753 m^2
Books, magazines, brochure	Offset lithography or relief printing	5,559,721,890 pieces
		270,729,319 m^2
Advertising	Digital or screen printing	1,443,524,728 pieces
		412,609,726 kg
		65,609,276 m^2
Packaging	Gravure or relief printing	3,166,230,640 pieces
		2,748,446 tons
		1,726,308,595 m^2
Business stationary	Offset lithography	6,735,642,459 pieces
		9,508 tons
Art prints, invitations etc.	Offset lithography or gravure	1,189,274,992 pieces
		1,059,381,744 m^2
		96,167,424 tons

CHAPTER THREE
HEALTH AND SAFETY IN PRINTING

The protection of the general public's health and safety is the duty of the state. Occupational health and safety policies are based on the 'user pays' principle, whereas the environmental policies tend to be based on the 'polluter pays' principle. Probably, both principles are more appropriately defined as 'risk creator pays' if they can be identified. This means that polluting enterprises have to assume responsibility and pay compensation for undesirable externalities associated with their operations. Accordingly, newly developed products have to be tested for their safety before being used. (Malich, Braun, Loullis, & Chris, 1998)

3.1 Key Principles in Occupational Health and Safety

A number of key principles underpin the field of occupational health and safety. Among these principles the vital objective is 'work should take place in a safe and healthy environment' (Alli, 2001).

Occupational health and safety is an extentive multidisciplinary field, invariably touching on issues related to, among other things, medicine and other scientific fields, law, technology, economics and concern specific to various industries. Despite these certain basic principles can be identified, including the following (Alli, 2001):

A-All workers have rights. Workers as well as employers and governments, must ensure that these rights are protected and foster decent conditions of labour. As the International Labour Conference stated in 1984:

a) work should take place in a safe and healthy working environment;
b) conditions of work should be consistent with workers' well being and human dignity;

c) work should offer real possibilities for personal achievement, self fulfilment and service to society.[1]

B-Occupational health and safety policies must be established. Such policies must be implemented at both the governmental and enterprise levels. They must be effectively communicated to all parties concerned.

C-There is need for consultation with the social partners (that is employers and workers) and other stakeholders. This should be done during formulation, implementation and review of such policies.

D-Prevention and protection must be the aim of occupational health and safety programmes and policies. Efforts must be focused on primary prevention at the workplace level. Workplaces and working environments should be planned and designed to be safe healthy.

E-Information is vital for the development and implementation of effecive programmes and policies. The collection and dissemination of accurate information on hazards and hazardous materials, surveillance of workplaces, monitoring of compliance with policies and good practices, and other related activities are central to the establishment and enforcement of effective policies.

F-Health promotion is a central element of occupational health practice. Efforts must be made to enhance workers 'physical, mental and social well-being'.

G-Occupational health services covering all workers should be established. Ideally, all workers in all categories of economic activity should have access to such services, which aim to protect and promote workers' health and improve working conditions.

[1]:conclusions concerning Future Action in the Field of Working Conditions and Environment, adopted by the 70th Session of the International Labour Conference on 26 June 1984 ,section I, paragraph 2.

H-Compensation, rehabilitation and curative services must be made available workers who suffer occupational injuries, accidents and work-related diseases. Action must be taken to minimize the consequences of occupational hazards.

I-Education and training are vital components of safe, healthy working environments. Workers and employers must be made aware of the importance and the means of establishing safe working procedures. Trainers must be trained in areas of special relevance to different industries, which have specific occupational health and safety concerns.

J-*Workers, employers and competent authorities have certain responsibilities, duties and obligations.* For example, workers must follow established safety procedures; employers must provide safe workplaces and ensure Access to fist aid; and the competent authorities must devise, communicate and periodically review and update ocupational health and safety policies.

K-*Policies must be enforced*. A system of inspection must be in place to secure compliance with occupational health and safety and other labour legislations.

3.1.1 Rights and duties

It is increasingly recognized that the protection of life and health at work is a fundamental workers right in other words, decent work implies safe work (Alli, 2001).

Furthermore, workers have a duty to take care of their own safety, as well as the safety of anyone who might be affected by what they do or fail to do. This implies a right to know and to stop work in the case of imminent danger to health or safety. In order to take care of their own health and safety, workers need to understand occupational risks and dangers. They should therefore be properly informed of hazards and adequately trained to carry out their tasks safely. To make progress in occupational health and safety within enterprises, workers and their representatives have to cooperate with employers, as well as to participate in elaborating and implementing preventive programmes.

The responsibilities of governments, employers and workers should be seen as complementary and mutually reinforcing to promote occupational health and safety to the greatest extent possible within the constraints of national conditions and practice.

Because occupational hazards arise at the workplace, it is the responsibility of employers to ensure that the working environment is safe and healthy. This means that they must prevent, and protect workers from, occupational risks. But employers' responsibility goes further, entailing a knowledge of occupational hazards and a commitment to ensure that management processes (Alli, 2001).

It has been maden some questionnaires among printer workers in order to see taking care of employees own health and safety that will be mentioned following chapters.

3.2. *Occupational Illness and Injury*

The World Health Organization (WHO) (2000) defines health as ‘a state of complete physical, mental, and social well-being and not merely the absence of disease, or infirmity’.

Occupational illness is any abnormal condition or disorder, other than one resulting from an occupational injury, caused by exposure to environmental factors associated with employment. It includes acute and chronic illnesses or diseases that may be caused by inhalation, absorption, ingestion, or direct contact.

Occupational injury is any such injury such as a cut, fracture, sprain, amputation, etc., which results from a work accident or from a single instantaneous exposure in the work environment (National Safety Council, 2007).

Occupational injuries are a major cause of preventable morbidity (and mortality) in men, especially in regions where work place health and safety standards are deficient (WHO, 2000).

Fundamental aims of occupational health is protection from occupational ilnesses. Occupational illnesses can be grouped in five (Özcan, 2001):

-come in to being with chemical substances
-skin illnesses,
-respiration system illnesses,
-contagious diseases,
-come in to being with physical factors

Especially we underscore occupational illnesses come in to being with chemical substances in this thesis.

Every year one thousand new chemicals are manufactured and enter the commercial bazaar, and this value is one hundred thousand in global measure. And these chemicals used unconsciously constitutes risk on human and environment health. According to 2001 formal statistics of Turkey, the number of illness developing from working life is 440 and the number of death is 1448. But against of these datas, ILO's scientific estimations emphasizes that the numbers of illness are 70 times and deaths are 20 times greater than to be known (Burgaz, Eke, & Orhan, 2007)

3.3 The Factor Affecting The Health Of Printing Workers

The factor affecting the health of printing workers are biological, physical, ergonomic, chemical, physicological and socio-cultural factors.

Biological factors can be defined as cleanliness; individual cleanliness (hand, body, clothing, work environment), and cleanliness tendency to products. Chemical factors such as organic solvents, alcohols and derivatives, pigments, acids and bases (İkizoğlu, 2003).

Ergonomic factors are lighting, heavy loadings, wrong and repetitious movements. Physical factors are noise, vibration, heat, light, humidity, ventilation, accidents (Özcan, 2001).

Physico-sociological factors: heavy working tempos, shift system,

A questionare was prepared to investigate and evaluate the health conditions of printing workers this was employed to the 139 workers in seven different printing offices. In this several questions were included such as general health rules, work accidents, chemicals used in printing industry, the factors affecting health in the printing environment. These are the some results of these questions (Özcan, 2001):

-The question of “what facts do you know harmful to health at a printing office?” majority gave the answer dangerous chemicals for human health, against lots of workers said noise, dust and deficiency at air condition.

-The answers given to the question of “which fact do you think is the most important for workers health?” Are; biological factors 56 %, physical factors 19 %, psychological factors 25 %.

-What kind of precaution against occupational disease and work accidents, majority said no precaution, some of the workers said by cleaning, using personal protector, giving education and using cautionary signal.

-The question of is there environmental measurement on working place against environment and human, and the question if there is biological analysis like blood test, urinalysis; some of the workers said yes 7 %, no 81 %, sometimes12 %.

-Workers are generally have avareness of health and destructive affects on health. % 69 of workers have avareness of dangerous chemicals for human health.

-Workers explained that biological factor is more important than physical and psychological factors.

According to the survey, in an office not only workers but also employers cause problems about health and it is standing out that employer doesn't take the necessary steps.

After this survey, Özcan (2001) classified preventive measures about chemical facts that destroys health at a printing office by within the framework of the survey answers below:

*General checkups and measuremets must be continously done. Periodical checkups must be done starting in work and during working life. Biological controls (pollution measurement on atmosphere, workers blood test, urinalysis) must be done on workers and environment. during working hours, disease breeding factors must be find out and cleaning must be done.

*Non destructive material and process must be used. Destructive materials should be out of usage at offices or those materials should be cahanged less destructive materials. The employer should follow up-to-date informations and should use non destructive materials or methods at office.

*In course of worker's employment, the office air should be air-conditioned and the conditioner should always be maintained.

* For chemical wastes precaution should be taken where chemical material put and chemical wastes should store seperately. Warning signs must put where wastes stored.

*Protective material should provided and the employer must make use of protective materials. Protective measurements should taken for workers.

*From the starting on a job, workers should be educated about office, work specification and chemical materials they are working on.

*Workers should be take under cleaning control, cleaning agent should provided and those materials should be checked.

*If there is bad physical and ergonomic factors that affects workers health negatively, it should be eliminated.

*Controlling is may be one of the most important fact on health. Employer should constitute a controlling group and make this group control the problems that threats the health.

In 2000, another survey has been maden about concentrated on chemicals in the workplace The Australian Council of Trade Unions (ACTU) conducts a survey of Health and Safety representatives every 2 years or so. In 167 returned surveys, respondents reported (Winder, Azzi, & Wagner, 2005):

• 88 % of respondents said they use chemicals at work,
• 33 % of respondents said that people at their workplaces have suffered health effects from chemicals at work,
• 75 % of respondents had not had training about the safe use of chemicals at work,
•66 % of respondents said they are aware of legislation and associated responsibilities,
• 23 % of respondents said that chemicals in theirworkplaces are not clearly labelled,

• 15 % of respondents said that the label is not easy to understand,
• most respondents did not know the difference between “poisons,” “hazardous substances” and “dangerous goods”,
• over 50 % of respondents believed that they have not been given adequate information about the chemicals in their workplace,
• 70 % of respondents indicated that they would like more information,
• 81 % of respondents said that not enough is being done by employers, employees and/or governments to ensure chemical safety at work,

3.3.1 Main Health Hazards in Printing

There are also some other health hazarsd except the chemicals hazards. The following Table 3.1 summarises the main health hazards in printing together with chemical hazards (Printing Industry Advisory Committee, 2007).

Table.3.1 Health hazards in printing (PIAC, 2007)

Hazard	Health effects	Typical processes
Inhalation of solvent vapor	Headaches, nausea Effects on the central nervous system	Running and cleaning lithographic and letterpress printing rollers and cylinders Screen, flexographic and gravure printing
Contact with and absorption of solvent through the skin	Dermatitis	All printing processes, especially cleaning of printing machinery
Inhalation of vapors and mists from isocyanates or reactive acrylates	Occupational asthma	Use of lacquers, adhesives or inks containing isocyanates or reactive acrylates (in UV inks)
Skin contact with reactive chemicals	Dermatitis including sensitization	Use of UV cured products Etching or engraving Platemaking Screen reclamation Stereo roller preparation Gravure cylinder preparation
Skin contact with and inhalation of potentially toxic or very toxic additives	Carcinogenic Mutagenic	General printing and cleaning activity involving the use of, e.g. font solutions, biocides, formaldehyde, dichloromethane, N-vinyl pyrrolidone (NVP)
Exposure to high levels of noise i.e. screen reclamation and radios	Noise induced deafness Tinnitus	Web printing Print finishing
Awkward and repetitive movements/manual handling	Back disorders	Handling of paper reels, sheets and bundles
Awkward or repetitive movements	Upper limb disorders, e.g. tenosynovitis and carpal tunnel syndrome	Typesetting Print finishing Book binding and packing
Exposure to micro organisms from contaminated water	Humidifier fever Legionnaires' disease	Paper storage of printing where humidifiers are used Any printing process in building with cooling towers or other water systems that can become contaminated

3.5 Exposure To Hazardous Chemicals

Chemicals are not all of equal concern. The assessment of health risks of chemical substances is a continuous process where information of the chemical hazards and exposure patterns are made available through a variety of sources (http://chemcareasia.wordpress.com/?s=inhalation, 2007).

No chemical substance can cause adverse effects without first entering the body or coming to contact with it. There are four main ways, that is routes of exposure, for chemical substances to enter the human body (http://chemcareasia.wordpress.com/?s=inhalation, 2007):

- Inhalation (breathing in)
- Absorption (through the skin or eyes)
- Ingestion (eating, swallowing)
- Transfer across the placenta of a pregnant woman to the unborn baby

Most chemicals used at the place of work may be dispersed into the air to form dust, mist, fumes, gas or vapour and can then be inhaled. In this way also workers who are not actually handling them but stay within the reach can be exposed to a mixture of chemicals from various sources.

Handling chemical substances without proper precautions exposes the worker to the risk of absorbing harmful amounts of chemical through the skin. This usually takes place when the chemical is handled in liquid form. Dust may also be absorbed through the skin if it is wetted by, for instance, sweat. The capacity of different chemical substances to penetrate the skin varies considerably. Some substances pass through it without creating any feeling. Skin absorption is, after inhalation, the second most common route through which occupational exposure may take place.

The protective external layer of skin may be softened (by toluene, dilute washing soda solution) thus permitting other chemicals to enter readily to the bloodstream (such as aniline, phenol, benzene).

Eyes may also absorb chemical substances, either from splashes or from vapours.

Dangerous chemicals can enter the body through ingestion as gases, dusts, vapours, fumes, liquids or solids. Inhaled dust may be swallowed, and food or cigarettes may be contaminated by dirty hands.

Eating, drinking and smoking should be prohibited at the place of work where dangerous chemicals are used.

Whatever the route of entry, chemicals can reach the blood stream and be distributed all over the body. In this way damage can be caused at the site of entry as well as to organs distant from the exposed area.

3.5.1 How Chemicals Affect Us

The harmful effects of chemical substances depend on the toxicity and the exposure to that chemical. Toxicity is a property of the chemical substance, while the exposure depends on the way the chemical is used. The level of exposure depends on the concentration of the hazardous chemical and on the period of contact time. Many substances do not give any warning by odour, even though they may be present at dangerous concentrations in the workplace air(http://chemcareasia.wordpress.com/?s=inhalation, 2007).

3.5.1.1 Acute effects - Chronic effects

The effects may be acute: after a short exposure an immediate effect may be experienced. Chronic effects usually require repeated exposure and a delay is observed between the first exposure and appearance of adverse health effects (http://chemcareasia.wordpress.com/?s=inhalation, 2007).

A substance may have acute and chronic effects. Both acute and chronic conditions can result in permanent injury.

Injury from exposure to a chemical substance can be temporary, i.e. reversible. It will disappear when exposure to that chemical stops.

Exposure to solvents may cause contact dermatitis, headache or nausea. These effects could be both acute and temporary. Solvents can also cause chronic effects and result in an irreversible, permanent injury to the nervous system.

3.5.1.2 Local effects - Systemic effects

Hazardous substances may cause local effects. Acute local effects may include corrosive injuries from acids and bases or lung injuries from inhaled gases such as ozone, phosgene and nitrogen oxides.

Many other gases cause adverse effects only after they have been inhaled repeatedly over a long time period. Low concentrations of a gas may also act in this way. A persistent irritation of the respiratory system can arise from exposure to gases such as sulphur oxides, hydrogen fluoride and hydrogen chloride.

Once the hazardous substance has entered the blood circulation, it may be distributed to all parts of the body. It will reach the liver, which is the most important detoxication organ of the body. The liver attempts to convert the toxic agents to a less toxic ones or to the ones useful to the body. This process is called metabolism. Some substances such as alcohol and carbon tetrachloride can damage the liver.

The body excretes unwanted chemicals. The kidneys filter them from blood circulation, which is the main way that the body excretes poisons, but in doing this, the kidneys can be damaged by toxic substances, such as carbon tetrachloride, ethylene glycol and carbon disulphide. Cadmium causes permanent damages to kidneys.

Other means of excretion are via faeces, sweat and through lung exhalation.

The nervous system is sensitive to chemicals. The adverse effects may be on the central nervous system or on the nerves that transport impulses to other parts of the body.

Organic solvents are commonly used at work and are known to be able to affect the nervous system. An example is tetraethyl lead, a gasoline additive, which causes skin effects at the contact site. Then it is absorbed and transported into the body causing typical effects on the central nervous system and on other organs.

Many other substances used in printing may behave in the same way, such as carbon disulphide, mercury, lead, manganese and arsenic.

Lead, in the form of the metal or its compounds, is another classic example of a chemical that may cause blood problems. Lead in the blood may inhibit certain enzyme activities involved in the production of hemoglobin in red blood cells. Chronic lead poisoning may result in a reduced ability of the blood to distribute oxygen throughout the body, a condition known as anaemia.

The liver is a purification plant which breaks down unwanted substances in the blood. Solvents such as carbon tetrachloride, chloroform and vinyl chloride, as well as alcohol, are hazardous to the liver.

The kidneys are part of the body's urinary system. They have the task of excreting waste products that the blood has transported from various organs of the body, of keeping the fluids in balance and of ensuring that they contain an adequate blend of necessary salts. They also maintain the acidity of the blood at a constant level.

Solvents may irritate and impair kidney function. The most hazardous to the kidneys is carbon tetrachloride used in printing. Turpentine in large quantities is also harmful to the kidneys: `painter's kidney' is a known condition related to occupational exposure. Other well-known kidney-damaging substances are lead and cadmium used in printing.

Our body has a considerable capacity to excrete, to render dangerous substances harmless, and to protect us. However, our defense system can be overloaded by repeated heavy exposure so that it no longer fulfills its function. The body may store the harmful substance which may consequently result in health problems.

Lead is an example of a substance for which removal from the body takes a long time. Cadmium is an example of a substance that will stay in the body once it has entered there.

3.5.2 Common Chemical Groups That Cause Health Risks

3.5.2.1 Dusts, fumes and gases

Dust may be just a nuisance, and the danger depends on the type of material in the dust, and on the amount and the size of the particles. The smaller the particle is the deeper it will penetrate into the lungs with the inhaled air, thereby passing the defensive systems of the lungs. This type of dust is invisible to the eye and identified using microscope technique. Such dust can accumulate in the lungs over a long period of time and cause a lung disease called pneumoconiosis. Dusts containing crystalline silica or asbestos most frequently can cause this condition (http://chemcareasia.wordpress.com/?s=inhalation, 2007).

Exposure to metal fumes can cause damage to the body. `Metal fume fever' is a known health effect when metal fumes, often containing zinc, are inhaled. It usually appears on the day following that of the exposure.

Sulphur oxides, nitrogen oxides, chlorine and ammonia are toxic gases that are corrosive and irritating to the respiratory system. They are widely used in industry.

Phosgene is formed when solvents containing chlorine, such as 1,1,1-trichloroethane and trichloroethylene, come into contact with hot surfaces or flames. Phosgene can be deadly poisonous even before the odour is detected.

3.5.2.2 Solvents

Most industrial solvents are liquid organic chemicals. They are used because of their ability to dissolve other substances, particularly fat and grease, which are insoluble in water. Many of them evaporate rapidly at ambient temperatures. They are often flammable and may ignite by heat from smoking, welding or static electricity. Vapours move with air currents and can ignite even by a distant heat source.

Inhalation is the most common way for solvents to enter the body, but some of them penetrate intact healthy skin. Once in the blood stream a solvent can be transported to different organs, such as the brain and liver.

Solvents have different effects on humans, depending on their evaporation rate and their solubility in water. The risks of health effects depend on the period of exposure and the concentration of the solvent in the inhaled air.

Many solvents have a narcotic effect; they may cause dizziness, headache, reduced comprehension or tiredness. They may also irritate the eyes and the respiratory tract. Frequent skin contact defats the protective layer of the skin causing irritation. Some solvents are very hazardous to the liver, kidneys, bone marrow or nervous system. Benzene, carbon tetrachloride and carbon disulphide belong to the category of solvents which should be substituted to less dangerous ones.

3.5.2.3 Metals

Metals can enter the body in the form of dust and fumes (in grinding or welding) or even through the skin.

Lead is used in various industries: battery, glass and mining industries, cable manufacturing, foundries and in printing works.

Chromium compounds, particularly chromates and bichromates, are widely used in industry. Cement contains small amounts of chromium compounds. These compounds can cause allergy and even lung cancer. Unlike cobalt and nickel, pure metallic chromium does not cause allergy.

Chromium compounds may cause birth defects if mothers are exposed to these compounds during pregnancy.

3.5.2.4 Acids and bases

Strong acids and bases are mostly used as water solutions. They are corrosive to human tissue. Working with acids or bases can give rise to mists which have the same corrosive properties as the solutions.

When acids and bases are mixed with each other the phenomena of neutralization occurs, usually with strong production of heat. The heat production has particularly serious effects when water is added to concentrated sulphuric acid: the heat will splash the highly corrosive liquid up.

Ammonia, sodium and potassium hydroxides are commonly used bases. They are corrosive to human tissue in such a way that a certain period of time is required before the corrosive feeling is sensed. Bases penetrate the skin and cause deep sores. They are difficult to wash away. Dilute water solutions are irritating.

Sodium and potassium hydroxides are used, for example, in hot degreasing baths for cleaning metals (http://chemcareasia.wordpress.com/?s=inhalation, 2007)

3.6 Investigation of Chemicals of Printing Industry and Their Health Effects

The printing industry involves many occupational exposures, including lead, organic and inorganic pigments, paper dust, adhesives, polycyclic aromatic hydrocarbons, acrylates, and solvents such as benzene, toluene, xylene, ethylene glycol, and carbontetrachloride. In 1996, IARC classified occupational exposures in printing processes as possibly carcinogenic to humans based mainly on reported excesses of bladder and lung cancer. (Bulbulyan, Ilychova, Zahm, Astashevsky,.& Zaridze, 1999)

Chemicals used in printing industry cause different serious health problems. For this reason many universities and companies has studied and investigated about these health problems in printing industry. Below some examples about these studies:

White, Proctor, Echeverria, Schweikert, & Feldman (1995) studied about neurobehavioral effects of acute and chronic mixed-solvent exposure in the screen printing industry. Industrial hygiene investigation identified the following chemical exposures as present: toluene, methyl ethyl ketone, mineral spirits, beta-ether, methylene chloride, and acetic acid. Results suggest that the mixed solvents used in the screen printing industry have an effect on central nervous system functioning in the absence of obvious clinical disease.

Bonig, & Karmaus (1999) studied about exposure to toluene in the printing industry is associated with subfecundity in women but not in men. Their aims is to examine the possible influence of exposure to toluene on human fertility. And conclusion of this study was low daily exposure to toluene in women seems to be associated with reduced fecundity. This result was in accordance with other findings for organic solvents and supports both the hypotheses that (a) organic solvents could affect hormonal regulation, and that (b) organic solvents increase early fetal losses which in turn contributes to longer times of unprotected intercourse.

Nise & Ørbæk (2006) studied about toluene in venous blood during and after work in rotogravure printing and toluene exposure was studied in 62 male rotogravure printers, employed in three plants. Toluene levels increased statictically significantly during the work week and the slow decrease of toluene in venous blood was followed in six workers for two weeks after cessation of exposure.

Crouch & Gressel (1999) studied the control of press cleaning solvent vapors in a small lithographic printing establishment and the ventilation system was found to be suitable for vapor and dust control, although substitution of a cleaning solution containing non-carcinogenic solvents for solutions containing carcinogens was recommended.

And also IARC (1996) determined the human carcinogenicity data in printing industry

Notwithstanding the variability in the results, there are indications of excess risks among printing process workers for some types of cancer. In its evaluation of these data, the Working Group considered the likelihood of publication bias, the possibility of confounding by cigarette smoking, and the imprecision and inconsistency of the designation of exposure groups. Based on these considerations, the Working Group concluded that there is weak evidence of an increased risk of lung and urinary bladder cancers among workers in the printing industry.

While there was a suggestion of an increased risk of lung and urinary bladder cancers in relation to exposure to printing inks, the quality of the data was weak.

The Working Group noted that the vast majority of epidemiological studies covered workers who were in the printing industry in North America or Europe during the middle of the twentieth century. Very few of the studies included workers whose employment was after 1980. Given the rapid technological changes that have gone on in this industry in North America and Europe in the past decade, it is questionable whether the exposure circumstances that were prevalent in the past are still prevalent. However, there may be areas of the world in which the older processes are still prevalent. Where the technologies have substantially changed from those of the past and insofar as this has changed the exposure conditions, the present evaluation may not be relevant.

No consistent association between employment in printing trades and morbidity from non-malignant diseases has been observed. Solvent-induced central nervous system damage has been observed in several but not all studies on employees in printing trades. Ultraviolet radiation-cured printing inks are a frequent cause of allergic contact dermatitis.

One study suggested that occupational exposures may induce hepatic damage in printers, but several other studies failed to confirm this finding.

Several pigments and dyes used in printing inks are mutagenic in *Salmonella typhimurium*: para red, dinitroaniline orange, azo dye D & C Red No. 9.

An increased frequency of chromosomal aberrations in peripheral lymphocytes in printing workers exposed to *inter alia* toluene was found in two studies, but not in two other studies. In one study, an increased frequency of chromosomal aberrations was found in workers exposed to toluene and benzene. In one study of a group exposed to toluene, an increased frequency of sister chromatid exchange was found, but not in two other studies.

In one study of printers exposed to lead, increased frequencies of chromosomal aberrations and sister chromatid exchange were found.

In one study, an increased frequency of micronuclei was observed in printing workers exposed to toluene. In one study of volunteers exposed to toluene, no increase in sister chromatid exchange was observed in lymphocytes.

As we can see that there is a clear relationship between hazardous chemicals used in printing and illnesses. It is undeniable realism.

3.7 Minimization of Health Impacts of Printing Chemicals

3.7.1 UV Printing

Nowadays there are innovations in printing like other sectors, and UV printing, UV cured inks and even UV cationic inks and lacquers have been developed.

The implementation of the 1990 Clean Air Act (CAA) has had a major effect on the coatings industry in terms of reducing Volatile Organic Compounds (VOCs). Ultraviolet (UV) curing coatings have emerged as one of the efficient vehicles to challenge the VOC limits in organic coatings . In addition, UV coatings also offer the advantages of fast curing speed, high energy efficiency, and low capital investment and space requirement. These coatings are especially suitable for the wood (furniture) or plastics coating, metal decorating, and paper printing industries. This is a consequence of an ambient temperature cure . There are two principle mechanisms in which the UV coatings polymerize on the substrates, free radical and cationic (Wua, Searsa, Souceka& Simonsickb, 1999). The most widely used in UV-radiation curing: acrylates, which polymerize by a radical mechanism, and epoxides, which polymerize by a cationic mechanism.

In free radical initiated polymerization, free radicals are generated using either unimolecular photoinitiators (benzoylketals) or bimolecular photoinitiators (thioxanthones). Multi-functional acrylate esters are used with acrylate functionalized oligomers to form highly crosslinked films. The functionality of the monomers can range from one to six functionality. To balance the reactivity and overall performance, a mixture of mono, di, and tri/higher functional monomers are commonly used. Free radical polymerization, however, exhibits oxygen inhibition of propagating radicals. In addition, acrylate monomers also represent odor problems, and more importantly, health hazards (Wua, Searsa, Souceka, & Simonsickb, 1999).

Acrylic UV-systems contain high molecular oligomers or prepolimers and also photoinitiators (i.e. benzophenon).

Although UV light drying technologies have already been in use for over 30 years in the printing industry, it is still considered as a new technology in comparison with conventional printing. Before UV-curing technologies, hazardous chemicals containing VOC’s and heavy metal pigments are used in printing, causing health problems on workers. Furthermore for 30 years chemical substances such as benzophenols, amines and acryclic acids have been used in conventional UV curing and these were also harmful for the people and environment.

In Turkey, since 1980, UV inks and lacquers are in use and some of these chemicals have hazardous characteristics. It is estimated that about 60-85 tons of UV-lacquers, 20-30 tons auxilary materials and 40-60 tons of cleaning solvents are used per month in Turkey. These figures indicate the importance of the problem. On the other hand, UV printing within the concept of cationic system with newly developed inks and lacquers are much more environmental friendly and the application of this technique is increasing in time. (Türkman, Akgün, Onuş, & Özman, 2005).

According to information obtained via personal communication in our country annual amount of UV inks and lacquers used in sector is showed in table 3.2.below:

Table 3.2 UV inks and lacquers used in Turkey

Consumption of UV ink and lacquers in Turkey	
UV inks	24 tonnes/year
UV lacquer	780 tonnes/year
UV-cleaning solvent	48 tonnes/year
Sum	852 tonnes/year

3.7.1.1 UV Offers An Environmental Advantage

UV technology utilizes monomer-based inks that have a solid composition and can be laid down heavily. While conventional inks dry by oxidation, UV inks are "cured" when hit by UV lighting after each color station on the press. This curing process happens almost instantly, and the paper absorbs less ink than in traditional printing. End results are crisp, detailed images with high print and color quality(Maitland, 2004).

High color quality on uncoated stock and nonporous substrates is one of the greatest benefits of UV printing. Traditional ink dries by oxidation; UV ink does not dry but is cured. Traditional ink is absorbed into uncoated stocks; UV ink cures onto the surface, resulting in a sharper, cleaner image. Conventional and UV curing mechanisms are showed in below figure 3.1.

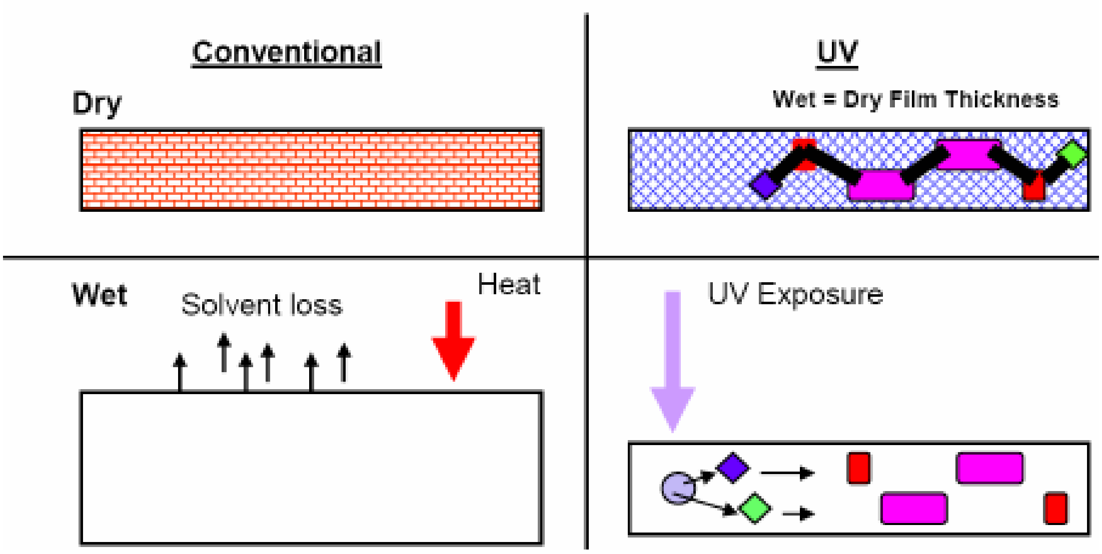


Figure 3.1 Conventional and UV curing mechanisms

In comparison to traditional inks, UV inks provide several environmental advantages. The curing of UV ink does not produce harmful by-products, like those in other ink systems Because UV inks eliminate solvents, VOCs (volatile organic compounds) are in turn eliminated from escape into the atmosphere. Sheetfed Advisor, Keith Kuebelbeck, says the inks are so environmentally sound that the empty ink containers can go directly into the recycling—no need for special disposal. In addition, UV cured materials can safely be recycled (Maitland, 2004).

3.7.1.2 UV Cationic Ink And Lacquers

Hazardous chemicals had affected people with their properties until UV-curing systems was found. To protect from harmful and hazardous chemicals and provide clean, green environment, especially after 1999/45/EC communicating, related to hazardous preparations, it has been started research and development studies in printing chemistry. For this reason cationic UV lacquers and inks development has been started. It is thought that these cationic UV printing inks and lacquers have non-hazardous properties.

Turkey has also started to follow the current developments in UV printing.

Recent and current developments in the design and synthesis of novel cationic photo-initiators, as well as new cationically polymerizable monomers, will contribute to increase and diversify further the use and development of the cationic radiation curing technology. A commercial diaryliodonium salt (referred to as DAI in the present paper) has just been introduced on the market by Ciba. At the end of this limited evaluation in both clear and pigmented systems, it is possible to conclude that this new cationic photoinitiator exhibits numerous benefits over current commercial onium salts, which are two-fold, being both:

Benefits derived from its chemical structure, such as:
-absence of heavy metal: PF6 anion;
-absence of non-substituted aryl ring.

Benefits derived from its chemical nature, such as easily indirectly activated by means of electron transfer sensitization or, eventually, photo-redox induced decomposition by free radicals (Carroy, Chomienne, & Nebout, 2001).

Although there is a number of niche alternative curing technologies, by far the most important is cationic curing. In terms of their use in food packaging applications, cationic curing inks are desirable because, in theory at least, the post-cure reaction will continue until all the monomer is consumed, thus minimising migration. A further significant advantage is the superior mechanical properties of cationic inks and coatings following post cure, allowing them to survive processes such as steam sterilisation and retorting which are becoming increasingly important in the food packaging sector. These advantages are countered by the cost, slow cure speed, weak inks, high odour on cure and humidity inhibition to the extent that their use is often too much of a compromise, particularly when competing against an established technology like free-radical. (Herlihy, Rowatt, & Davidson, 1996).

UV-cationic-curing, based on the photo-generation of acid and consecutive cationic polymerization, was first proposed in 1970s. Since then, wide variety of cationically polymerizable monomers, such as epoxides and vinyl ether derivatives, has been investigated. Among these, formulations based on cycloaliphatic epoxy resins (such as 3,4-epoxycyclohexyl- 3_,4_-epoxycyclohexane-carboxylate: ECC) are known to give cured coatings with high thermal capability, excellent adhesion and good chemical resistance. The curing rate of ECC is rather high, but still much lower than that for radical ones. Thus, it has been desired to develop novel cationic formulations keeping the good performance capabilities, while at the same time possessing higher reactivity competitive with radical system (Sasaki, 2007).

For cationic UV polymerization, typical initiators are triarylsulfonium, diaryliodonium, and aryldiazonium salts. Of the three, aryldiazonium salts are less widely used because of low thermal-stability, and evolution of nitrogen during the photolysis (Wu, Sears, Soucek & Simonsick, 1999).

After 1999/45/EEC, European Union countries have started research and development to reduce the human exposure to hazardous chemicals. From these studies reactive UV-Cationic inks and lacquers were formulated with properties of nearly zero migration rates and no VOC content. EU directives propose these UV-Cationic inks and lacquers. These cationic UV printing ink and lacquers and chemicals also have less hazardous properties. Table 3.3summarizes the properties of cationic UV inks and lacquers.

Table 3.3 Cationic UV-inks and Lacquers (Türkman, Akgün, Onuş, & Özman, 2005).

Color pigments	Organic pigments have no heavy metals.
Bindings	Resins, cycloaliphatic epoxy vinyls
Solvents	No VOC
Oils	None
Additives matters	Drying agents: photoinitiators (pure types) Plasticisers: polyols (pure types) Surface reformatory (pure types) Foam preventive (pure types)

Recent and current developments in the design and synthesis of novel cationic photo-initiators as well as new cationically polymerizable monomers will contribute to increase and diversify further the use and development of the cationic radiation curing technology (Carroy, Chomienne, & Nebout, 2001).

In general, the epoxy components of the cationic UV inks are less reactive than acrylate systems. Lower press speeds are the consequence.

The excellent performance of the UV curing process is further enhanced by the use of cationic systems based on cycloaliphatic epoxides. Cycloaliphatic epoxides rapidly polymerize in the presence of strong cationic initiators. Stable onium salt photoinitiators have been developed that undergo photolysis in the presence of ultraviolet light to form a highly efficient cationic species. These photoinitiators can be combined with cycloaliphatic epoxides to provide coatings systems that are storage-stable until activated with UV light. Systems containing these photoinitiators have proved to be stable for more than two years when not exposed to ultraviolet light.(The Dow Chemical Company)

What are Photoinitiators?

A photoinitiator is a compound especially added to a formulation to convert absorbed light energy, UV or visible light, into chemical energy in the form of initiating species, free radicals or cations. Cationic photoinitiators are used extensively in optical lithography. The ability of some types of cationic photoinitiators to serve as latent photochemical sources of very strong protonic or Lewis acids is the basis for their use in photoimaging applications.

Aldrich offers a large selection of photoinitiators of various chemical classes acetophenone, benzil/benzoin, benzophenone, thioxanthone, onium salts, and others.

Photoinitiators are additives which use energy from ultraviolet or visible light to induce polymerisation, or to cure, as the case of in coatings and inks; that is, they are used to dry a coating through the application of light rather than heat. An ink or coating containing a photoinitiator can dry in less than a second under a UV light. UV curing results in several benefits to the customer. In the first place, these coatings and inks are virtually solvent-free; they emit no volatile materials when they dry. UV curing uses less energy than conventional curing, and the resulting coatings have high gloss and scratch resistance (Aldrich, 2005).

3.7.2 Health And Safety In UV Printing

Health and safety is an important issue to be carefully considered when using UV drying technology. Some of the potential hazards involved are the same as with conventional printing techniques; the use of cleaning solvents and generation of ink-fly from fast-moving ink rollers. Ink-fly derived from UV printing technology contains uncured polymer components which are classed as irritants and potential sensitisers (Edmonson, 2000).

Dust hazards are generally lower for UV drying technology since spray powders are eliminated as the printed ink is virtually dried instantaneously by UV light.

Additional hazards, not encountered in conventional printing, are associated with the UV light sources. Ozone is generated by reaction of UV light on air near the lamps and generally removed from the printing machine by means of Local Exhaust Ventilation (LEV).

UV light is a potential hazard to both eyes and skin from inadequately protected UV sources. UV lamps are adequately shielded during manufacture, but it is possible for "hot-spots" to be visible, due to the non-replacement of worn rubber seals. This situation may or may not be hazardous. All UV sources should be considered, including laboratory small-scale machines, as well as the large-scale printing machines.

UV drying technology is successfully used by a growing number of printers without any health and safety problems at all, and this is attributed to good working practices and a serious respect for health and safety issues and regular assessments of the hazards involved.

Ultraviolet (UV) light is a small part of the overall electromagnetic spectrum, lying between 10 and 400nm wavelength. UV light between 200nm and 315/320nm is termed as the UV Actinic Region and this is the region which represents the greatest hazard to humans. The biological effects of over exposure to UV light are dependent on the wavelength of the light, but since penetration of the light is small, the eff Ultraviolet light is a particular portion of the light spectrum, typically considered to be in the wavelength range from 200 nm (nanometers) to 400 nm. Light in this spectral range has many important uses including water purification, semiconductor lithography, sun tanning and, of course, adhesive curing.

Since ultraviolet light falls below the visible portion of the light spectrum, we cannot see pure UV light. This can be an important consideration, because another significant property of light is its *intensity*. Special equipment—a radiometer—is required to measure the intensity of UV light. The intensity of light falling on a surface is measured in milliwatts per square centimeter (mW/cm^2), or power (mW) per unit area (cm^2).

3.7.2.1 Health effects of UV Printing

Effects to the skin

Over exposure leads to two effects, short-lived (acute) effects experienced within a few hours of exposure, and long-term (chronic) effects, which may not appear for several years. The acute effects produce sunburn. The redness produced is termed erythema and is caused by light shorter than 315 nm. The severity of the effect is dependent on the duration and intensity of the exposure; dark skins have a higher threshold to developing severe erythema than fair skins. Exposure promotes tanning and thickens the skin, both of which increase protection (Edmonson, 2000).

Chronic effects of over exposure to UV light can include premature skin ageing and, potentially, skin cancer. As with erythema, the most important wavelengths appear to be those below 315 nm. There is now correlation between atmospheric UV light and skin cancer, particularly with the fairer white population(Edmonson, 2000).

Effects to the eye

Over exposure leads to kerato-conjunctivitis, alsa known as "arc-eye", "welders' flash" or "snowblindness". Pain, similar to that resulting from grit in the eyes, as well as an aversion to bright lights is characteristic of the symptoms. The cornea and conjunctiva show inflammatory changes. As with the skin effects, permanent corneal damage is rare.

The maximum effect on the eye for a given exposure is produced at a wavelength of 270 nm. Absorption of UV light in the lens is thought to contribute towards its progressing yellowing with increasing age and to be a factor in producing cataracts.

3.7.3 Health and Safety Management Plan in Printing Industry

Safety and health management systems are a way to organise and design procedures and processes in organisations in such a way that all requirements in terms of employees' safety and health are fulfilled on the basis of the applicable safety and health legislation. These can be the ways for any printing industry which hazardous chemicals are used in:

3.7.3.1 Technical Measures to Control the Hazard

Technical measures can be used to prevent chemical hazards at source. By technical means it is possible to reduce the exposure of the worker. Effective control method for any hazardous chemical is substitution: a hazardous chemical is replaced with a less hazardous one. This is especially important when the chemicals in question can cause cancer, damage to the reproductive functions or create allergic reactions.

Choosing a safer process or changing an old and hazardous process to a less dangerous one effectively reduces the risks.

An example of safer choice is to have pellets or paste instead of powdered substances which readily produce high levels of dangerous dusts. Water-based paints and adhesives are available to replace harmful products containing solvents.

All possible information should be made available when considering the change of a substance or the whole process so that the new choice does not create unexpected new dangers(http://chemcareasia.wordpress.com/?s=inhalation)

3.7.3.2 Closed System

If hazardous chemicals can not be replaced by less dangerous ones, exposure must be prevented by protecting the worker. Enclosing the hazardous process or chemical is an effective method.

One example is to use sealed pipes to transfer solvents and other liquids instead of pouring them in the open air. Vapours and gases caused by spray painting or produced in pickling or hardening baths in the metal industry should be controlled, ventilated and not allowed to enter the workplace air (http://chemcareasia.wordpress.com/?s=inhalation).

3.7.3.3 Local Exhaust Ventilation

It is not always possible to enclose all dangerous operations. A properly designed local exhaust ventilation is the second choice in order to remove the contaminants at the source. A local exhaust ventilation system consists of a hood, ducts or pipes, a system to collect and separate the pollutants from the clean air, and an efficient fan to create enough suction force (http://chemcareasia.wordpress.com/?s=inhalation).

The hazardous gases, fumes and dust can be collected from the vented air. They should not go untreated, straight out, to pollute the surroundings of the factory and the environment.

Attention should be paid to the clean air inflow which replaces the exhaust. Inspection, proper maintenance, regular cleaning and changing of filters are essential to protect the workers against hazardous contaminants.

3.7.3.4 General Ventilation

Where it is difficult or impossible to prevent hazardous chemicals, fumes, dusts, mists or particles from entering the workplace air at the source, a general dilution ventilation can be installed. This should be designed to meet the needs of the specific work process and workplace. At its best it should consist of an inflow of clean air and an outflow of exhaust forced by fans at right places. It can also be used with other preventive measures (http://chemcareasia.wordpress.com/?s=inhalation).

3.7.3.5 Housekeeping

When working with dangerous chemicals, proper housekeeping is essential. Storage areas must be well organized and kept in order. The transport of chemicals within the industrial premises should be planned and the transport routes kept clear. Maintenance of premises and equipment should also be planned. These tasks should be dedicated to appointed persons/work groups/departments. Workers using the equipment should know the person responsible for repairing faulty equipment. Monitoring the efficiency of housekeeping and inspections should be carried out regularly; this should involve the workers themselves, who are experts in their own work.

3.7.3.6 At Places of Work

A Code of Practice has been developed by the International Labour Organisation, and some countries have applied these principles for organizing hazard control. This may involve the following activities at the shop-floor level: Safety Committee could initiate to

- do regular inspection using checklists made for the particular chemicals and chemical processes in use;
- mark and label all chemicals;
- keep at hand an inventory list of all chemicals handled in the place of work together with a collection of Chemical Safety Data Sheets for these chemicals;

- train workers to read and understand the Chemical Safety Information, including the health hazards and routes of exposure; train them to handle dangerous chemicals and processes with respect;
- plan, develop and choose the safe working procedures;
- reduce the number of people coming into contact with dangerous chemicals;
- reduce the length of time and/or frequency of exposure of workers to dangerous chemicals;
- train workers to know and understand the emergency procedures;
- equip and train workers to use personal protective equipment properly after everything possible has been done to eliminate hazards by means of other methods;

3.7.3.7 Storage

Planning and proper maintaining of storage areas is very relevant for users of chemicals in order to avoid material losses, accidents and disasters. Hazardous substances can leak, cause a fire or give off dangerous fumes and vapours. When two substances come into contact with one another, they may react violently. The reaction products may be much more dangerous than the original chemicals.

Special attention should be paid to incompatible substances, suitable location of products within the storage area and proper arrangements and climatic conditions.

For example, cylinders should be fixed with chains to upright position; the acids in the area or cupboard meant only for them. The acid fumes or splashes should never reach the area where cylinders are kept.

Written instructions of storage practices should be provided, and Chemical Safety Data Sheets of dangerous substances kept in the stock, and should be available in the storage area.

CHAPTER FOUR
LEGAL FRAMEWORKS ABOUT PRINTING

4.1 Legal Framework

The enactment of regulations for the efficient control of chemical substances has been enforced mainly because of two developments in recent years. First, the number of chemicals produced or used by industry, which have the potential to affect human health or the environment, has grown steadily. Second, incidents of harm to workers, to public health or to the environment have increased. The rationale for a standardised policy for the safe handling, supply, and use of hazardous substances has not been only injuries, diseases, fatal incidents and rising costs, but the increasing environmental awareness of the public as well.

With the widespread utilisation of chemicals and hazardous substances, the legal requirements for controlling their supply, handling, and use are getting more extensive. (Malich, Braun, Loullis & Chris, 1998).

In general, chemicals used in printing industry are hazardous. Their uses are limited with directives, especially European Union's (EU) directives try to limit hazardous chemical.

4.1.1 EU Aproach

The legal framework of the European chemicals sector has a rather long record towards the harmonisation of different Member States regulations. These were dealing mainly with questions of labelling, classification and packaging. The first European wide legislation came into force in 1967 with directive 67/548/EEC. From the perspective of the protection of human health and environment, the sixth amendment of the directive of 1981 is of interest, as it introduced a notification procedure for new substances, including test requirements. The seventh amendment of 1992 increased those requirements and introduced principles for risk assessment (Little, 2004).

European Union (EU) has regulated many directives and standards about minimization of hazardous chemicals used in industries. Some of them are given below:

a) 67/548/EU (Classification and Labeling of Dangerous Substances Directive)
b) 88/379/EU (Classification and Labeling of Dangerous Substances Preparation Directive)
c)93/112/EU (EU Safety Data Sheet Directive)
d)76/769/EEC (Dangerous substances and preparations legislation)

For printing inks which are intended to use for packaging many additional regulations have to be applied furthermore.

These regulations cover, consumer protection, environment, forbidden substances, special country ordinances, quality assurance, purity, waste and regulations which are given by associations and workers unions.

Manufacturing and Sales of Printing Inks require a number of regulations to be followed Standards and Regulations. As printing inks are chemical preparations the same general laws and regulations which are valid for chemical substances have to be applied (http://www.sunchemical.ch/umweltschutz).

-*CEPE Exclusion List for printing inks and related products*

A list of hazardous or banned substances which are never used in Printing inks. This list is a recommendation of the European Council of Paint, Printing ink and Artists' Colours Industry.

For some years a number of National Association members of European Council of Paint, Printing Ink and Artist Colors Industry (CEPE) have been independently composing voluntary recommendations for the exclusion of certain raw materials (substances and preparations according to the definition given in the Dangerous Substances Directive 67/548/EU) from printing inks and related products. These exclusion lists of materials have been based on health and safety matters in the day-to-day production and marketing of printing inks and associated products employing Good Manufacturing Practices. CEPE exclusion list has been mentioned in chapter 2 (CEPE, 2001).

The CEPE exclusion list will be under frequent review by the European Technical Commitee Printing Inks and may be amended where appropriate, in the light of new data on safety, health and environmental matters.

4.1.1.1 White Paper and REACH

On 13th February, 2001, the European Commission adopted a White Paper setting out the strategy for a future Community Policy for Chemicals. The main objective of the new Chemical Strategy is to ensure a high level of protection for human health and the environment, while ensuring the efficient functioning of the internal market and stimulating innovation and competitiveness in the chemical industry. Commenting on today's announcement Environment Commissioner Margot Wallström said: "This is one of the most important initiatives the Commission has taken in the context of sustainable development. We have decided on a step-by-step approach to phase out and substitute the most dangerous substances – the ones that cause cancer, accumulate in our bodies and in our environment and affect our ability to reproduce. This decision is crucial for future generations" (http://europa.eu.int/comm/environment/chemicals/reach.htm).

The Commission proposed a new EU regulatory framework for the Registration, Evaluation and Authorization of Chemicals (REACH) on 29 October 2003. The aim is to improve the protection of human health and the environment through the better and earlier identification of the properties of chemical substances. At the same time, innovative capability and competitiveness of the EU chemicals industry should be enhanced. The benefits of the REACH system will come gradually, as more and more substances are phased into REACH.

The REACH proposal gives greater responsibility to industry to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers will be required to gather information on the properties of their substances, which will help them manage them safely, and to register the information in a central database. A Chemicals Agency will act as the central point in the REACH system: it will run the databases necessary to operate the system, co-ordinate the in-depth evaluation of suspicious chemicals and run a public database in which consumers and professionals can find hazard information

REACH will cover approximately 30,000 chemicals produced and imported into the EU in amounts of one metric ton or more a year, equivalent to nearly a third of the total number of chemicals available in Europe. Around 5 to 10 percent of the chemicals or substances in the REACH plan are considered to be so dangerous that they will have to go through an authorization procedure, the outcome of which could be enforced substitution by safer alternatives. As a result, ink makers could find that some key chemicals they use will no longer be available and that they will have to go through the costly exercise of reformulating some of their inks. The first substitutions could take place within a few years “Some chemical companies with products which will have to be authorized may want to start replacing them as soon as possible,” said Jacques Warnon, technical director at the European trade association for coatings (CEPE), which includes the European Printing Inks Association (EuPIA).What has been excluded from the agreement between the parliament and EU governments could also be as significant as what has been included. Ink companies had been hoping that the legislation would make clear that the main responsibility for gathering safety data for the registration of substances would rest with the chemical manufacturers. Registration of substances will have to include information on their uses as well as data on their chemical and other characteristics. Under REACH, chemicals needing possible substitution will be those categorized as being carcinogenic, mutagenic and toxic for reproduction (CMRs), persistent, bioaccumulative and toxic (PBTs) and very persistent and very bioaccumulative (vPvBs) (Milmo, 2007).

As a result of the compromise, use of these chemicals will only be allowed when safer and economical alternatives are not available. Adequate control will also have to be demonstrated to ensure the chemicals remain within approved safety thresholds.

Dangerous substances without safety thresholds will only be authorized if a social-economic analysis (SEA) shows that the benefits of their continued availability on the market outweighs the effects of a ban. A key part of the deal is an obligation on applicants for authorizations to submit substitution plans giving details of how they hope to replace the chemicals with safer alternatives.

CEPE fears that a relatively large number of chemicals contained in existing inks and coatings formulations may ultimately be substituted.

“Several hundred chemicals used in inks and coatings may have to be replaced,” said Mr. Warnon. “This could be difficult for SMEs because they will need time to find alternatives which are less dangerous while they will require resources to do all the necessary testing of replacements.”

In a recent report, Frost & Sullivan, the market research organization, warned that a large proportion of the substances used in the manufacture of a typical ink may no longer be available because of REACH.

It stated that in the inkjet ink sector, the registration costs of the raw materials would account for nearly 5 percent of sales. An average reformulation would take a company 35 days, including time for the creation of a new recipe and its testing. The development of new formulations would need five to 10 staff per ink company, according to Frost & Sullivan.

One of the key issues for chemical producers and ink producers over the next few years will be how these registration costs will be shared out. Suppliers and users will have to work closely together to make sure the registration process operates smoothly (Milmo, 2007).

4.1.2 UV Protocol

The German Berufsgenossenschaft Druck und Papierverarbeitung– Institution for statutory accident insurance and prevention in the printing and paper processing industry – as well as the British Health and Safety Executive (HSE), the French Caisse Nationale de l'Assurance Maladie des Travailleurs Salariés (CNAMTS) and the Italian Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro (ISPESL)- have already taken major steps in chemical safety assessment. Together, these institutions provide a reliable European platform which aims to reduce the amount of VOC's (volatile organic compounds) used in the printing industry.

One successful example of this European platform is the UV Protocol, which covers the safe use of UV printing technology in the graphics industry (Rad-tech Europe, 2006).

The protocol describes the risks involved when using UV drying inks and specifies respective safety measures**.** One of the advantages of UV Technology is that the printing ink cannot dry in the ink duct but immediately on the appropriate substrate, if the ink is irradiated with UV light. Compared with other printing processes a higher brilliance and abrasion resistance can be achieved. The UV technology offers also advantages from the view of health protection: The ink doesn't contain solvents and there is no need for the use of print powder because of the immediate drying (Sprotte, 2001).

However, the advantages for health protection become only effective, if all demands of health and safety are considered.

The UV Protocol looks at hazards such as :

- Skin irritation - or in extreme cases, sensitisation, which can lead to sever allergic reaction through contact with UV inks
- Inhalation of ink mist or fly, which can cause respiratory sensitisation
- Contact with wash-up solvents
- Inhalation of ozone, which can lead to irritation or nausea

- Exposure to UV light may irritate the eyes or burn the skin

As to the precautions described in the protocol, measures can be considered already at the design stage of the machine, for example avoidance of mist from ink or lacquer building up. But the protocol also provides the user with a number of useful safety measures for easy application such as the use of protective clothing. The UV protocol specifies: "For these cleaning procedures, operators should wear gloves. For example, disposable nitryl gloves may be worn. When solvents are used, unlined, solvent-resistant neoprene gloves must be worn. Care should be taken that gloves with a good overlap of the sleeves of overalls are used. For longer periods of exposure, or for mechanical processes, neoprene or nitryl gloves with a thickness of at least 0.4 mm should be worn. Damaged or degraded gloves, i.e. gloves that have lost their shape, elasticity or colour, must be replaced in all cases.

If protective clothing is contaminated with a small amount of UV curable resin, then it should be removed and the material cured by exposure to daylight as a low-level UV source. If clothing is severely contaminated then it should be disposed of safely. Work clothing should be stored separately from personal clothing and should not be taken home for laundering."

The UV protocol also describes safe working practices: "Waste cleaning materials such as for example contaminated wipes etc. should be disposed of in dedicated, specially labelled bins and in accordance with local waste disposal regulations. Hazard-free procedures must be developed for clearing jams in the machines in all places where there is a danger of exposure to uncured UV inks. Operators are to be issued suitable equipment for personal protection and instructed in its use. Automatic cleaning systems should preferably be installed for cleaning processes within the press. If any machine parts, e.g. ink wash-up trays, regularly need to be removed for cleaning, a suitable work space is to be provided with local exhaust ventilation for gasses released and a facility for draining off liquids." The importance of regular health surveillance is also stressed in the protocol.

Reduce emissions

According to Mr. Mike Wilcock from the British Health and Safety Executive (HSE), the overall aim of European partnership is to reduce emission of any kind in general. The introduction of solvent-free UV inks is in Wilcock's view one of the possibilities to reduce solvent emission. Special attention should, however, also be given to washing and cleaning agents. All endeavours in this respect have been pioneered by the institution for statutory accident insurance and prevention in the printing and paper processing industry with their industry-wide initiative for the reduction of solvent use in offset printing. It was due to this industry-wide initiative that in Germany the share of volatile solvents sank from 61 % to 36 % from 1995 to 2000. Based on this success, a respective initiative was started in the UK in 2000 where similar results (Sprotte, 2001).

4.1.3 UVITECT Project

The UVITECH project (2004) is a notable example of European member states working together to solve common problems in the printing industry. The programme was funded under the European Commission's "Growth Programme.

UVITECHT Project complements the joint UV Protocol. It is explained that there are needs about exposure with hazardous chemicals, occupational health and safety and environmental views that should be stressed in UV-curing systems.

This project was aimed at addressing the inequality found in the printing industry experienced by SME printers over the introduction of UV curing technology. Printers are aware of the economic and technical advantages of this technology, as well as the safety implications of using polymer systems containing acrylates. The aim was to assess the risks, using high-quality measurements, from inkfly produced from UV printing and compare it with other risks associated from this type of printing.

It identifies the hazards and offers practical advice on how to minimise the risks associated with printing both with UV and conventional inks.

4.1.4 Control of Substances Hazardous to Health (COSHH) in the Printing Industry

The Health and Safety Commission is responsible for health and safety regulation in Great Britain. The Health and Safety Executive and local government are the enforcing authorities who work in support of the Commission. The use of hazardous substances at work is subject to the Control of substances hazardous to Health Regulations, COSHH.

The UK Control of Substances Hazardous to Health Regulations places a responsibility on employers to do all that is reasonably practicable to ensure the safety of their employees and to protect them from harmful substances. In addition, the COSHH Regulations include some requirements related to the suppliers' duties. The COSHH Regulations also include general requirements from the primary legislation the UK Health and Safety at Work Act 1974 for employers, owners of premises and others such as contractors (Malich, Braun, Loullis, &, Chris, 1998).

Print workers are exposed to a range of hazardous substances, including chemicals during the course of their work. Information on how to reduce exposure to chemical agents is contained in COSHH Essentials for Printers.

What is required?

Under COSHH you must :

-Assess the risk to health arising from the use of hazardous substances at work.

-Prevent or control the risk of exposure

-Ensure that control measures are used and maintained

-Monitor exposure and undertake health surveillance as necessary

-Inform,instruct and train all exposed employees-and others e.g., third parties on site –about the hazards, risks and controls

-Keep records of assessments, maintenance, monitoring, health surveillance and training.
-Compile a full list of all substances in use within the workplace, and obtain all relevant material safety data sheets (MSDSs) from suppliers

These requirements are explained in details below:

COSHH Assesments

It is the process of evaluating the risks to health from a substance and deciding on the action needed to reduce or control those risks.

The responsibility to carry out the assessment rests with the employer, through the task can be given to somebody who has the ability to get all the required information and make the correct decisions about the risks and the precautions required. They need to understand the regulations as well as the Approved Code of Practice on COSHH.

When carrying out the assessment it is important that they consult with managers and employees representatives so they understand the work and the risk involved. Do not focus entirely on the substances that you buy. Look at the main process in each area and consider what the main exposures are.

*Think of the measures that are currently in place and consider their effectiveness.
*Consider the work routines and the lenghts of time that people, including non-employees, are exposed
*Think about the effects of the substances if they were to cause harm (both acute and chronic)
*Consider how to exposure might occur. Could it be breathed in or will it be swallowed as a result of contamination to hands or clothing?
*Could there be exposure through accidental leakage, spillage or during maintenance?

*Evaluate the risks and come to some conclusions on what is needed to adequately control the risks.

You may find that many of the measures necessary to control the risks are already provided, but in any case, you should write down the conclusions of your assessment. You need to review the assessment from time to time to check that they remain valid. All assessments should be reviewed and revised at least every 5 years.

Control Measures

The purpose of the assessment is to decide what measures are needed to control the health risks presented by the substances.

The best and most reliably effective control measures must be considered first. Only if the better control measures are not reasonably practicable or will not be effective should the next lower standard of control be considered. The general hierarchy of control measures is as follows:

*total enclosure of the process, seperating the substances from the person, i,e., risk avoidance.
*substitution of the hazardous substances by one less hazardous
*partial enclosure or local exhaust ventilation (LEV)
*good general ventilation
*personal protective equipment such as respirators, gloves and goggles.

Other measures might include prohibiting eating, drinking and smoking in contaminated areas; providing facilities for washing and changing clothes as well as cleaning of the workplace.

Maintenance

The COSHH Regulations require that the control measures are kept in an efficient working order and good repair. If the control measures are engineering controls such as local exhaust ventilation (LEV), they should be examined by a competent person. In most cases LEVs need too examined every 14 months, usually by engineering insurance companies. Respirators and breathing apparatus also have to be examined more frequently, at least every 3 months.

Monitoring of Exposure

For certain substances, where there is a risk to health through inhalation, occupational exposure limits (OELs) have been set. These are published and updated annually in the HSE's Guidance Note EH 40 "Occupational Exposure Limits'', available via HSE Boks.

The OEL value should be compared with exposure levels in the workplace-via environmental monitoring techniques- to see whether exposure to the hazardous substance is being properly controlled. Such monitoring records shoul be kept for 40 years.

Health Surveillance

For some employees, health surveillance needs to be carried out if a known health effect due to exposure to the substances could be reasonably anticipated and observed. Records need to be kept of any health surveillance carried out for a period of 40 years.

Information, Instruction and Training

Employees must be provided with information about the risks to their health to which they are exposed; the measures that control that exposure and any monitoring or health surveillance that has been carried out. They should be instructed in what they need to do control these dangers and trained in how to use them.

4.1.5 US Approach

Manufacturing and Sales of Printing Inks require a number of regulations to be followed Standards and Regulations. As printing inks are chemical preparations the same general laws and regulations which are valid for chemical substances have to be applied (http://www.sunchemical.ch/umweltschutz, 2007)

FDA Approval

Although customers very often asked for this compliance FDA does not apply for printing inks. An FDA approval for printing inks can not be given.

Food and Consumer Goods Law. For printing inks the paragraphs 30, 31 with prohibitions and purity requirements are important. In the recommendation IX heavy metal limit values are given.

An early conceptual framework for controlling hazardous substances transmitted through food in the USA was the Federal Food and Drugs Act of 1906. In the 1970s, there was a development of regulatory law, resulting from the exponential rise in chemical production. The US Congress enacted in 1970 the Occupational Safety and Health Act and in 1976 the Toxic Substances Control Act TSCA The peculiarity of the US law hierarchy is the absence of a regulation for the safe handling of chemicals at the same legislative level as it exists in the other countries. An appropriate legislation exists at the level of nonstatutory law and is called the Federal Hazard Communication Standard HCS 1910.1200 13. Another standard concerning the control of hazardous substances is the Occupational Safety and Health Administration Laboratory Standard 1910. 1450, which applies especially for chemical laboratories. As with most nonstatutory legislation, employers do not have to comply with these performance-oriented standards, if they have efficient alternative solutions for achieving the required level of safety. Standard-setting procedures for the control of hazardous substances in the USA are initialised by

Occupational Safety and Health Administration OSHA or commence in response to petitions from other parties, including the Secretary of Health and Human Services, the National Institute for Occupational Safety and Health NIOSH, State Governments and others. The USA provides the most generous opportunities for the public to participate in regulatory proceedings (Malich, Braun, Loullis, & Chris, 1998).

United States Environmental Protection Agency (EPA) defines hazardous substances in terms of the characteristics. There is also Toxic Substance Control Act (TSCA) (originally passed in 1976 and subsequently amended) which applies to the manufacturers, processors, importers, distributors, users and disposers of chemical substances or their mixtures.

Another regulation that is related to the printing and publishing industry is EPA Toxic Release Inventory (EPA, 1995). It includes toxic chemicals released from printing and publishing industries. Table 4 1 gives the list of toxic chemicals used in printing industry and also included in TRI.

Table 4.1 Chemicals used in printing industry that are listed in the TRI.

Toxic Chemicals	
Acetone	Ammonia
Barium	Cadmium
Chromium	Copper*
Cumene	Cyclohexane
Methylene chloride	Ethylbenzene
Ehtyleneglycol	Ethylene oxide
Formaldehyde	Freon 113
Hdrochloric acid	Hydroquinone
Lead	Methanol
Methyl ethyl ketone	Methyl isobutyl ketone
Phosphoric acid	Silver
Toluene	Tetrachloroethylene
1,1,1-trichloroethane	Trichloroethylene
	Xylene

* copper phthalocyanine pigments delisted in May 1991

4.1.6 Turkish Legislations

4.1.6.1 Health and Safety Regulations in Printing in Turkey

In Turkey, after Ministry of Environment was established in 1991, many regulations has come into force.

With the 6th of the November in 2001 chronogram and 24575 numbered decision in formal newspaper, "Hazardous Chemicals Regulation'' was publicated. And 4th item of this regulation includes some chemical properties used in Printing and Package Industry:

1-Flammable substances 2-Highly toxic substances 3-Harmful substances 4-Corrosive substances 5-Irritative substances 6-Allergic substances 7-Carcinogenic substances 8-Mutagen substances 9-Heavy metal pigments and fillings

In the last 2-3 years, also many regulations related occupational health and safety have been put into force in Turkey. Some of the related regulations are given below:

-Procedures Related to Preparations of Materials Safety Data Sheets (Official Gazette, 11/03/2002, No: 24692)
-The Labour Law (4857 numbered Official Gazette, 10/06/2003, 25134) (article: 77, 78)
-Regulation on Occupational Health and Safety (Official Gazette, 09/12/2003, No: 25311)
-Regulation on Health and Safety Precautions When Working with Chemicals (Official Gazette, 26/12/2003, No: 25328)
-Regulation on Health and Safety Precautions When Working with Carcinogen and Mutagen Substances (Official Gazette, 26/12/2003, No: 25328)
-Regulation on Protecting the Workers from Hazards of the Explosive Substances. (Official Gazette, 26/12/2003, No: 25328)
-Regulation on Usage of Personal Safety Equipment at Work (Official Gazette, 11/02/2004, No: 5370)

The application of these rules and regulations will cause an important improvement in workers health and safety in many sectors including printing.

Except that the innovation of the chemicals and directives about these non hazardous chemicals there are also some regulations and studies about occupational health and safety.

In our country there are varies of regulations about ocupational health and safety. The appendix of “Regulation on Health and Safety Precautions When Working with Chemicals” includes occupatıonal exposure limits. Below, occupational exposure limits of chemicals, which are used in printing industry, are given in Table 4.2 and 4.3 according to Appendix-I/B and Appendix –I/C.

Table 4.2 Occupatıonal Exposure Limits according to Appendix– I/ B(*)

EINECS (1)	CAS (2)	Substance Name	Limit Value				Special sign
			TWA (4) (8 hours)		STEL (5) (15 min.)		
			mg/m3 (6)	ppm (7)	mg/m3	ppm	
200-467-2	60-29-7	Diethylether	308	100	616	200	-
200-662-2	67-64-1	Acetone	1210	500	-	-	-
200-834-7	75-04-7	Ethylamine	9,4	5	-	-	-
201-159-0	78-93-3	Butanon	600	200	900	300	-
202-422-2	95-47-6	o-Xylene	221	50	442	100	skin
202-704-5	98-82-8	Cumene	100	20	250	50	skin
202-849-4	100-41-4	Ethylbenzene	442	100	884	200	skin
203-473-3	107-21-1	Ethyleneglycol	52	20	104	40	skin
203-628-5	108-90-7	Chlorobenzene	47	10	94	20	-
203-631-1	108-94-1	Cyclohexanon	40,8	10	81,6	20	skin
204-065-8	115-10-6	Dimethylether	1920	1000	-	-	-
215-535-7	1330-20-7	Xylene (mixture isomers, pure)	221	50	442	100	skin
231-131-3	7440-22-4	Silver (Metalic)	0,1	-	-	-	-
231-595-7	7647-01-0	Hydrogen chloride	8	5	15	10	-
231-633-2	7664-38-2	Orthophosphoric acid	1	-	2	-	-
231-635-3	7664-41-7	Ammonia	14	20	36	50	-

(*) : Appendix of 2000 / 39 / EC numbered Directives

(1) EINECS : European ınventory of chemical substance

(2) CAS : Service record number of chemical substances .

(3) Specific sign: 'skin sign'', it represents taken into body through the skin

(4) TWA : Time-Weighted Average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

(5) STEL : Short term exposure limit is defined as a 15- minute TWA exposure which could not be exceeded at any time during a workday.

(6) mg/m^3 : amounts of substances in miligram that is in 1 m^3 of air at 20 ^OC 101,3 Kpa

(7) ppm : amounts of substances in mililitre that is in 1 m^3 of mililitre (ml/m^3).

Table 4.3 Occupatıonal Exposure Lımıt Appendıx– I / C (*)

EINECS (1)	CAS (2)	Substance Name	Limit Value (3)	
			mg/m³ (4)	ppm (5)
2 005 791	64-18-6	Formic acid	9	5
2 005 807	64-19-7	Asethic acid	25	10
2 006 596	67-56-1	Methanol	260	200
2 037 163	109-89-7	Diethylamine	30	10
2 151 373	1305-62-0	Calciumdihidyroxide (6)	5	-

(*) : Appendix of 1991 / 322 / EC numbered directive
(1) EINECS : European Inventory of Chemical Substances
(2) CAS : Service record number of chemical substances .
(3) Limit Value : Values measured or calculated according to 8 hours reference time
(4) mg/m^3 : Amounts of substances in miligram that is in 1 m^3 of air at 20 ^{O}C 101,3 Kpa
(5) ppm : Amounts of substances in mililitre that is in 1 m^3 of mililitre (ml/m^3).
(6) : Substances have limited scientific datas about health effects.

Regulations on Occupational Health and Safety in National Legislation

• Regulation on Occupational Safety and Health - 89/391/EEC
• Regulation on Health and Safety Measures for Working with Display Screen Equipment - 90/270/EEC
• Regulation on Vibration - 2002/44/EC
• Regulation on Noise - 2003/10/EC
• Regulation on Health and Safety at Construction Sites - 92/57/EEC
• Regulation on Health and Safety Signs - 92/58/EEC
• Regulation on the Use of Personal Protective Equipment at the Workplace by Workers - 89/686/EEC

Regulations on OHS in National Legislation

• Regulation on Health and Safety Measures to be Taken in the Buildings and the Extensions of the Workplace - **89/654/EEC**
• Regulation on the Use of Personal Protective Equipments at the Workplace by the Workers - **89/656/EEC**
• Regulation on Health and Safety Conditions for Fixed Term and Temporary Workers **91/383/EEC**

4.1.6.2 REACH On The Chemical Industry In Turkey

Turkish chemical industry consist of firms of various sizes. According to numbers stated in 2005, there were 20,623 firms operating in the Turkish Chemical Industry. As we can understand that chemical industry is very big industry and so is printing (Gürdal, 2006).

Plastics in primary forms and of synthetic rubber facilities In 2004, the value of Turkish Chemical Industry's total production was 10 Billion USD which accounted for the 4.3 % of GDP in Turkey (Gürdal, 2006).

The chemical industry accounts for almost 10 % of Turkey's GDP (World Bank 2004) and 30 % of the manufacturing output.

• The total value of imports by the chemical industry was 19.6 Billion USD while exports were 3.7 Billion USD.

In order to provide sufficient protection for human health and the environment to the potential harmful effects of chemicals while maintaining the economic benefits of chemicals development, the EU introduced a chemicals policy based testing and risk assessment of substances, information dissemination to the users of chemicals and the general public and restrictive measures for the most dangerous chemicals.

In order to fully implement the EU chemicals policy in Turkey as a part of its accession process to European Union, a technical assistance project funded by EU has been executed in Turkey. This project, provided technical assistance to the main involved institutions, especially the Ministry of Environment and Forestry (MoEF) to enable effective implementation of EU chemicals legislation

TeACH: (**Te**chnical **A**ssistance Project in the field of **Ch**emicals) Technical Assistance Project for Strengthening the Institutional Structure and Capacity in the Field of Chemicals for Turkey (MoEF, 2007).

Overall project objective:

The project's overall objective was to ensure high level of protection of the human health and environment from the hazardous effects of chemicals by developing and strengthening the existing chemicals management system in Turkey.

The project aims at developing the Turkish chemicals management system to make it fully comply with the EU requirements, as part of the EU accession process. This objective was realized through the implementation of the specific EU Directives in the field of chemicals and the establishment of the necessary system, the institutional structure and capacity, and the legal framework and by strengthening the regulatory cycle for implementation of the two key EU Chemicals Directives in Turkey (67/548/EEC and 1999/45/EC) and two of their daughter directives (91/155/EEC and 93/67/EEC).

The following new Turkish By-Laws and their annexes were prepared to fully transpose the above EU Directives;

1. By-Law on Classification, Labelling and Packaging of Dangerous Substances and Preparations,
2. By Law on Inventory, Notification and Risk Assessment of Substances,
3. By-Law on the Preparation and Distribution of Safety Data Sheets (SDS),

4. By-Law on Restriction of the Production, Placing on the Market and Use of Certain Dangerous Substances, Preparations and Articles.

The above legislation was prepared in close consultation with the ministries, governmental organisations, NGOs and industries.

1. Legal framework prepared and agreed among the involved institutions including the draft by-laws;
2. Institutional framework prepared and agreed;
3. Approximation Strategy on Chemicals revised and prepared with four main directives which are studied within this project.

CHAPTER FIVE
MIGRATION

5.1 Packaging Industry

Food and packaging are two unseperated topics such systems that are used for safe food protection not only act as a guideline for food manufacturers but also for their suppliers. Packaging is prolongation of printing, there are two types of packaging; internal and external packaging. Internal packaging come in to contact with food directly (Sükan, 2003).

Types of packaging: paper inclusive package (paper, board, card board) plastic inclusive package, glass, aluminium, tins woods. Sub types of them are; bags, paper bags, board boxes, fiber tubes, tin boxes, fiber barrels, pressurized packages, head pieces, bags (Sükan, 2003).

Today packaging consumption and production across the world is about 50 billion per anum in terms of value and about 1500 billion tons in terms of volume (Sükan, 2003).

5.1.1 Hazards of Packaging Materials In Contact With Foods

Together with the development of packaging industry, it has been started to use various chemicals at the production of different packaging materials. Today several anionic and cationic polymers, optical brightners, biocides, antifoaming agents, adhesives, solvents, printing pigments and inks are used for the production of paper and cardboard packaging materials. At the production of tin or metal packaging materials; various surface treatment chemicals, primers, binders, solvents, resins, paints, printing pigments and inks are used. Also for the production of glass and plastics packaging materials, different chemicals are used (Pocas & Hogg, 2007).

Monitoring exposure to these chemicals has become an integral part of ensuring the safety of the food supply. Human exposure to chemicals from packaging and other materials in contact with food may occur as a result of migration from the packaging materials into foodstuffs (Pocas & Hogg, 2007).

5.1.2 Interactions Between Food And Printed Packaging

The interactions between food and packaging include permeation, migration, invisible setoff and substance transfer in the enclosed air space of the packaging. (Huber Group, 2002)

Permeation is the transport of a substance through the packaging. Substances are thus able to pass from the environment to the package contents and vice versa.

Migration refers to the transfer of a substance from the packaging to the foodstuff inside and vice versa. The concentration of migrants is specified in mg/dm^3 of packaging or mg/kg of foodstuff (package contents).

Invisible setoff can occur in the stack or on the reel subsequent to printing. In a form invisible to the human eye, there is a possibility of low-molecular substances being able to transfer to the side of the packaging that will come into contact with the package contents.

From the physical point of view, permeation and migration are founded on the same subprocesses of distribution (solubility) and diffusion of transportable substances in the area of contact between packaging and foodstuffs. With respect to interaction between inks, packaging materials and foodstuffs, only migration and invisible setoff are of importance (Huber Group, 2002).

For minimisation of migration studies abot inks and curing technologies made. An important issue associated with substrates printed with UV inks is to ensure that the ink does not transfer out of the packaging. It is vitally important for the food packaging (Huber Group, 2002).

For the last 20 years, consumers' exposure to chemicals from food packaging materials has attracted much public attention and interest of European regulation authorities because somewhat high concentration levels of substances released by packaging materials were found in several food articles including, in particular, plasticizers released from poly (vinyl chloride) (PVC) cling-films or printing inks and bisphenols or derived compounds with epoxy or chlorhydrin group released from can coatings/varnishes, polycarbonate bottles, and sealants. Such molecules are known to be potentially carcinogenetic to humans and endocrine disruptors (Vitrac, & Hayert, 2005).

Migration from paper and board packaging materials has not been as extensively studied as migration from plastic materials.

Most of the migrants detected originated from the printing inks or adhesives used in the manufacture of the finished packaging. Diisopropylnaphthalenes (DIPNs) are an exception, because although they are used as solvents in some printing inks, they are also widely employed in the paper industry in the manufacture of carbonless copy paper and thermal paper.

The risks of contamination of food from printing ink components in packaging materials are associated with two mechanisms: transfer through the packaging material and set-off phenomena. The latter means that printing ink components are transferred from the printed to the non-printed surface by direct contact during the material's manufacture, storage or use. It should be noted that these phenomena usually involve substances other than dyes, and are therefore not visible (Aurela, 2001).

Although there is a number of niche alternative curing technologies, by far the most important is cationic curing. In terms of their use in food packaging applications, cationic curing inks are desirable because, in theory at least, the post-cure reaction will continue until all the monomer is consumed, thus minimising migration. A further significant advantage is the superior mechanical properties of cationic inks and coatings following post cure, allowing them to survive processes such as steam sterilisation and retorting which are becoming increasingly important in the food packaging sector. These advantages are countered by the cost, slow cure speed, weak inks, high odour on cure and humidity inhibition to the extent that their use is often too much of a compromise, particularly when competing against an established technology like free-radical. (Herlihy, Rowatt, & Davidson, 1996).

5.1.3 Packaging Materials And Migration

The substances that may migrate and that may affect the safety of the food obviously depend on the nature of the packaging material. The constant introduction of novel packaging materials has increased the number of specific hazards to which humans are exposed via the migration from packaging into food (Pocas & Hogg, 2007).

Synthetic polymers typically have high molecular weights (5000-1 million D) and therefore their biological availability is negligible. However, due to the use of lower molecular weight (<1000D) additives in these polymers as well as the presence of trace levels of unreacted monomers, there is a finite potential for human exposure to these lower molecular weight components. Substances that may migrate from plastic materials include monomers and starting substances, catalysts, solvents and additives. This latter class includes antioxidants, antistatics, antifogging agents, slip additives, plasticizers, heat stabilisers, dyes and pigments (Pocas & Hogg, 2007).

Paper and board are essentially composed of pulp from different vegetable sources and are most often employed in contact with dry foods. Additives used in this type of material include fillers, starch and derivatives, wet strength sizing agents, retention aids, biocides, fluorescent whitening agents and grease-proofing agents. Paper and board may also be coated with polymers as polyethylene or waxes. Recycled fibre is considered a major source of migrants. This route of contamination is officially recognised in the Resolution RESAP (2002) of the Council of Europe for paper and board in contact with foods, which lists DIPNs, benzophenone, partially hydrogenated terphenyls, solvents, phthalates, azo-colourants, primary aromatic amines and polycyclic aromatic hydrocarbons as being relevant. Corrugated board is most often used as transport packaging system and thus not anticipated to come into direct contact with food. However, volatile substances in this type of material used as a secondary package may be transferred through the primary packaging into the food (Pocas & Hogg, 2007).

Metal cans are made of tin-plate (steel coated with tin), tin-free steel (steel coated with chromium and chromiumoxides) or aluminium. Tin-plate is most used for food cans and aluminium for beverage cans. Most cans are internally coated with a polymeric layer, and thus the layer of food contact is not the metal but the lacquer. The substances of concern in can systems are therefore not only the metals involved, but also components migrating from the coatings, such as starting substances and their potential derivatives. Migrants from can coatings, namely phenolic resins, often contain only small amounts of monomers, oligomers and additives, but a large amount of other unknown or undescribed components (Pocas & Hogg, 2007).

As can been seen, there is a great variety of chemicals involved and an often complex mixture of migrants. Additionally, the migrant species may not be the substance used in the production or conversion of the material, but an unknown reaction product. Non-intentionally added substances, like degradation products from additives or monomers and impurities, and substances originated in printing inks, adhesives, solvents, etc. may also migrate into the food under certain conditions One of the current issues is the uncertainty in the identity and/or in the biological properties of the migrating substances non-identified and non-detected substances represent an uncharacterised contribution to the exposure of contaminants from food-contact materials (Pocas & Hogg, 2007).

The concentration of the migrants in the packaged food depends on (Huber Group, 2002):

• the initial concentration of the migrant in the printed packaging
• the speed with which the migrant migrates (diffusion speed)
• the equilibrium of distribution of the migrant, that is, its solubility in the printed packaging and in the foodstuff.

And also heat, contact time, food characteristics (oily, dilute, watery or acidic forms), mass state of foods (grain, powder, liquid, or paste state), physical and chemical cahracteristics of printing and packaging materials, concerns of products element to migrants or amount of materials that ready to migration are other important factors about migration speed and size (Tuncel &Üçüncü, 2002).

Triantafyllou, Akrida-Demertzi, & Demertzis, (2007) had maden investigations. Results showed the ability of selected contaminants of various types and various volatilities to potentially transfer to dry foods. The proportion of substances migrated to food was strongly dependent on the nature of the paper samples, fat content of the food, chemical nature and volatility of the migrant. The highest level of migration of organic pollutants was observed for the substrate with the highest fat content. Furthermore, it is shown that contact time and temperature have a significant effect on migration of model contaminants into foods.

Silva et. al. (2007) made study and this study's results indicate that storage temperature has greater effect on the values of the coefficient diffusion, whereas the fat content has a greater effect on the values of the partition coefficient KP/F. However, in addition other physico-chemical properties of fatty foodstuffs, such as water or protein content, may further affect the key parameters in migration phenomena.

To evaluate the effect of the fat content and of the temperature of storage on the migration from plastics packaging films into meat products as an important class of foodstuffs, the kinetic mass transport of a model migrant (diphenylbutadiene) from low density polyethylene (LDPE) film in contact with different meat products was investigated. From the data, the diffusion coefficients were calculated for the applied test conditions, by use of a mathematical model. (Silva, Cruz, Garcı´a, Franz, &Losada 2007)

The results showed that migration increased with fat content and storage temperature. Analysis of migration data corresponding to minced pork meat containing different amounts of fat, stored for 10 days at 25 ^{0}C, revealed an excellent relationship between migration level and fat content. This behaviour was also found for other types of meat products (chicken and pork neck).A simplifying mathematical model was applied to derive effective diffusion coefficients in the polymer which, however, do take kinetic effects in the meat also into account. In the case of pork meat contact, the effective diffusion coefficients derived from mathematical modelling were ten times higher for storage at 25 ^{0}C (1.88 x 10^{-9} cm^{2} s^{-1}) than for storage at 5 ^{0}C (1.2x 10^{-10} cm^{2} s^{-1}). (Silva et. al., 2007)

Migration of low molecular weight substances into foodstuffs is a subject of increasing interest and an important aspect of food packaging because of the possible hazardous effects on human health. The migration of a model substance (diphenylbutadiene) from low-density polyethylene (LDPE) was studied in foodstuffs with high fat contents: chocolate, chocolate spread and margarines (containing 61% and 80% fat). A simplifying mathematical model based on Fick's diffusion equation for mass transport processes from plastics was used to derive effective diffusion coefficients which take also kinetic effects in the foods into account and to determine partition coefficients between plastic and food. With this model migration levels obtainable under other storage conditions can be predicted. The effective diffusion coefficients for both margarines stored at 5 ^{0}C (3.0–4.2 x10^{-10} cm^{2} s^{-1}) and at 25 ^{0}C (3.7¯5,1 10^{-9} cm^{2} s^{-1}) were similar to each other, lower than for chocolate spread stored at 5 ^{0}C (9.1x 10^{-10} cm^{2} s^{-1}) and higher than the diffusion coefficient for chocolate stored at 25 ^{0}C (2.9x 10^{-10} cm^{2} s^{-1}). Good agreement was found between the experimental and the estimated data, allowing validation of this model for predicting diffusion processes in foodstuffs with high fat contents. (Silva, et al, 2007).

The maximum concentration of a migrant arises in the medium in which it best dissolves. In order to protect the consumer, we must make absolutely certain that he/she does not suffer from any impairment in the quality of the edible product or from detrimental effects on his/her health caused by the migration of constituents from the packaging to the foodstuff.

In the event of specific migration concentrations in a packaging/foodstuff combination being exceeded or toxicologically unevaluated migrants being transferred,

• other combinations of materials are necessary
• functional barriers that prevent migration must be used.

Paper and folding boxboard do not act as a barrier to migrants. In contrast to an all-purpose barrier, such as one made of coated aluminium, other functional barriers are impermeable only for specific classes of material.

5.1.4 Conformity of Foodstuff Packages

There is no all-purpose combination of ink and substrate for manufacturing foodstuff packages. It is only possible to satisfy all statutory arrangements relating to consumer protection and wishes with regard to the design of packages by employing a wide range of materials. Consequently, when choosing the raw materials to be used to manufacture packaging and the inks and varnishes that match them, it is essential that you know• what type of foodstuff is to be packaged• under what conditions the packaged foodstuff is to be stored or further processed (sterilisation, baking over, microwave oven)• where the packaging is to be marketed. Responsibility for the packaging rests with the manufacturer and packer. However, it is only possible to reach a satisfactory solution for new packaging development projects through co-operation between all suppliers, the manufacturer and the packer. This is the only way you can ensure that all the necessary information is available and the actions to be derived from this information can be put into effect. The challenge is just as much that of the substrate supplier as it is that of the ink manufacturer. But without knowing what the intended packaging goals are, neither of them is in a position to tender practicable recommendations. Whatever the case, the ink manufacturer takes from the outset all measures possible to provide the greatest degree of consumer protection possible (Huber group, 2002).

Due to the wide range of demands made on printing inks and varnishes with respect to the various printing processes and substrates, it is not possible to formulate an all-purpose ink that satisfies all packaging goals. This is why it is essential to make appropriate enquiries with the ink and varnish manufacturer when actually defining the specific procedures rather than leaving it until, for example, problems arise when using standard printing inks on micro-corrugated board packages. As mentioned below, the statutory framework actually makes it easier to design packaging of all kinds. When this framework is conformed to, the packaging can be used by the consumer without any risk. If in doubt or if the necessary data about packaging materials is not available, it is always possible to submit a particular type of packaging to a recognised institute for individual testing to verify its harmlessness. The calculation model ("migration modelling") introduced with the 6th amendment to plastics Directive 90/128/EEC (namely Directive 2001/62/EC, Art. 5, dated 9 August 2001) makes it possible to calculate the migration potential of a given composition of packaging material when those components of an ink that are capable of migrating are known. This migration modelling makes it far easier to check whether or not a particular packaging/foodstuff combination actually conforms to the relevant statutes.

5.2 Methodologies for exposure assessment

5.2.1 Analytical Methodology

Analytical methods are important because they are the keys in studying the migration of packaging components from the package or food-contacting material into the food. They are also required by regulatory agencies who are responsible for ensuring public safety by monitoring foods for excessive and potentially harmful levels of contaminants from the packaging. Furthermore, methodology is required to establish databases to evaluate changing residue levels as well as to calculate dietary intakes. Indeed, in the literature, most of the related analytical work was reported with one of the following objectives(Lau & Wong, 2000):

(a) to identify the potential migrants or contaminants in the food contact packaging materials and access their toxicological potency,

(b) to determine levels of residual monomers or additives in food contact materials and in foods with which they had been in contact,

(c) to identify the factors affecting the migration of contaminants from the packaging into foodstuff, and

(d) to estimate the maximum likely intake of the contaminants resulting from the food contact usage. (Lau & Wong, 2000)

The choice of method for carrying out an exposure assessment is influenced by the purpose of the exercise, the nature of the chemical, and the resources and data available. When estimating chemical exposure,four basic guiding principles should be followed:

-the estimate should be appropriate for the purpose,
-the estimate should have an assessment of accuracy,
-any underlying assumptions should be stated clearly and
-critical groups of the population should be taken into account when these groups are disproportionally affected by the chemical.

The differences between food additives (direct) and substances migrating from packaging (referred to in a US context as ‘‘indirect additives’’) are such that they require different methodologies when assessing consumer exposure to them. When the substance in question is not a direct food chemical, such as food additive, natural toxin or pesticide residue, but a chemical migrating from the packaging system, additional information is needed on the nature and composition of the packaging materials, the types of packages used for certain foods (related to packaging usage factors) and data on migration levels of the substance in question. Exposure, in a dietary context, is defined as the amount of a certain substance that is consumed and is usually expressed as the amount of substance per mass of consumer body weight per day. The general model to describe the exposure to chemicals from food packaging can be represented as:

Exposure (mg/person/day)= Concentration (mg/kg_{food})*Food Consumption (kg_{food}/person/day)

where concentration represents the concentration of the chemical that contaminates the food. Food Consumption represents the intake of food packed in a certain type of packaging system that contains the migrating chemical. Alternatively, exposure can be expressed in terms of the amount of packaging used which contains the chemical in question.

Exposure (mg/person/day) = Migration(mg/dm^2)*Packaging Usage (dm^2/person/day)

where Migration represents the amount of chemical migrating into the food. The migration level depends on several variables such as the packaging material itself, the chemical and physical nature of the food in contact, the initial concentration of the substance in the packaging material, time and temperature, and it also depends on the ratio of surface area of packaging material to the amount of food product.

For assessing the exposure to packaging chemicals, it is necessary to know what type of food (chemical and physical nature) is packaged in what type of material, as this determines the presence and concentration of the chemical and influences the potential for migration into the type of food. For example, considering the consumption of mineral water, the chemicals migrating from polyethylene terephthalate (PET) bottles are certainly different from those migrating into the same mineral water packaged in PC bottles. On the other hand, if the migration from PET bottles is considered, the migration value of a certain substance will be different if we consider a soft drink (acid in nature) instead of a mineral water.

Another factor to be considered in linking packaging usage, food consumption and migration data is the ratio of surface area of the packaging to volume of food product. Mass transfer of the chemical is a surface area phenomena and the concentration achieved in the food or food simulant depends on its volume or mass. Therefore, the size and format of the packages are also very important. The European legislation system assumes that 1 kg of food is exposed to 6 dm^2, but the current trend to smaller portions and therefore smaller packages, points to the need for revising this assumed value of surface area to volume ratio

5.2.2 Migration Limits

These limits can be found in the ‘positive lists’ mentioned above. The terms defined for these limits are (Huber Group, 2002):

Global migration (GM) The entire quantity of substances that is allowed to pass from a consumer good to a foodstuff during the contact time with the foodstuff, expressed in mg/kg.

QM Maximum concentration of a toxicologically evaluated substance in the packaging material, ex-pressed in mg/kg.

SML Specific Migration Limit; i.e. the concentration (expressed in mg/dm^2) of a toxicologically evaluated substance, which must not be exceeded in foodstuffs or in food simulants (SML = ADI x 60).

ADI Acceptable Daily Intake, expressed in mg/kg; i.e. the quantity of a toxicologically evaluated substance that may be consumed with foodstuffs on a daily basis without risk to health (toxicological concentration limit x safety factor of 100).

The Overall Migration Limit OML may be seen as a restriction of food contamination by the sum of the substances migrating from food contact materials. It is not related to food safety: on the one hand it is too high to exclude the presence of migrants which may endanger human health; on the other, an OM exceeding the limit is not indicative of a risk. Food safety must be ensured through the control of the migrating components. The OML cannot be derived scientifically. It should be as low as technically possible, taking into account that organic materials cannot be produced free of low molecular weight material potentially migrating into food. Further, it should be coherent with tolerated food contamination from other sources: there should not be strict (and costly) limits for contaminants from one source, while far larger amounts are tolerated or not even investigated from others, e.g., packaging. By convention, the European limit is 60 mg/ kg, which is far higher than nearly all limits for other foodcontaminants (Grob, Biedermann, Scherbaum, Roth, &Rieger, 2005).

SMLs are a risk management tool derived from toxicological data, such as tolerable daily intakes (TDIs), or from a limited toxicological assessment ensuring safety only for a low migration. As the exposure of consumers cannot be calculated from consumption data (the open European system does not restrict the use of a given authorized substance), a worst case is assumed: 1 kg of food packed in materials releasing the substance in question at the SML is consumed per day.

However, deviation from this conservative assumption by a conversion from the limits in terms of concentration in food or food simulant to units per contact surface area may strongly reduce the amount of food that can be eaten to reach the TDI. Furthermore, the EU is about to introduce the fat consumption reduction factor (FRF), taking into account that on a long term average virtually nobody consumes more than 200 g fat per day: when food contains more than 20% fat, the measured migration is divided by the FRF, the percentage of fat divided by 20, i.e. by 5 if the food consists of pure fat. The FRF does not apply to the overall migration (OM).

Migration per contact surface area for the manufacturers of packaging materials, limits in terms of concentrations of migrants in food may be a problem when it is unknown how much food the material will ontact. Small amounts of food are generally in contact with more packaging material (higher surface area / volume) and, therefore, concentrations in food tend to be higher the smaller the portion.

Industry wants to be protected against extreme requirements in the case of a small amount of food in contact with an extremely large packaging surface area. They would argue that foods packed in small portions are usually consumed in small amounts. These are reasons to express SMLs and the OML as limit per food contact surface area. The European legislation assumes that 1 kg of food is exposed to 6 dm^2 surface area of packing material, i.e. that it forms a 1 kg cube. Accordingly, the OML of 60 mg/kg is equivalent to 10 mg/dm^2. This is also an extreme assumption: while it is a good approximation for 1 kg packs of flour or rice, for example, for most foods the contact surface area is substantially larger and, therefore, the tolerated migration in terms of concentration is higher. European legislation specifies that OM and SM should be determined as concentrations in food if the packaging material can be filled (known surface area/volume ratio) and has a volume between 0.5 and 10 l (Directive 2002/ 72, Article 2). For small containers, the limits apply as migration per surface area. If the packaging material cannot be filled, i.e. if it is, for example, a sheet or film, the ratio of contact surface area/volume is unknown and limits always apply as migration per unit surface area in food contact, i.e. as mg/dm^2. This means that for the majority of packs the limits apply as amounts per contact surface area and, thus, the conversion factor of 6 dm^2/kg is used—which is why this conversion factor is so important. It also means that SMLs are not really based on the consumption of 1 kg of food, but on the amount of food which is in contact with 6 dm^2, which is mostly far less than 1 kg in real life. (Grob, Pfenninger, Pohl, Laso, Imhof, Rieger & 2005).

5.2.3 Migration Test

The basis is council directive 82/711/EEC and the subsequent amended directives laying down the basic rules necessary for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. These directives lay down basic rules for migration tests conducted to determine the overall migration and the specific migration of individual substances using food simulants and under defined test conditions. Since it is not always possible to use real foodstuffs when testing materials that come into contact with foodstuffs, food simulants are used. By convention, these are classified in one or more foodstuff categories according to their character. Here is a list of food simulants as stipulated in EU directive 85/572/EEC (Huber Group, 2002):

Foodstuff categories and food simulants		
Foodstuff category	**Food simulant**	**Abbreviation**
1. Aqueous foodstuffs (pH >4.5)	Distilled water	Food simulant A
2. Acidic foodstuffs	3% acetic acid (G/V) (aqueous foodstuffs with a pH > 4.5)	Food simulant B
3. Alcoholic foodstuffs	10% ethanol (V/V) (adjusted concentration)	Food simulant C
4. Fatty foodstuffs	Olive oil	Food simulant D
(5.) Fatty foodstuffs	Tenax (powder) ENV 1186-13 (for card stocks)	

Figure 5.1 Foodstuff categories and food simulants

5.2.3.1 Simulation

For reasons of analytical feasibility, migration may be determined using food simulants A–D, respectively water, 3% acetic acid, 10% ethanol or olive oil, depending on the nature of the food. Testing conditions are standardized (EU Directives 82/711/EEC and 85/572 EEC). Basically the system of simulation assumes worst cases of real use in order to ensure that migration into food does not exceed that in since simulant D (olive oil) often extracts more efficiently than fatty foods, a reduction factor was introduced, today called simulant D reduction factor (DRF), to distinguish it from the FRF. The DRF should avoid strong overestimation of migration into food and implies that migration (overall or specific) is divided by a factor of up to 5 before it is compared to the legal limit. For cheese, the DRF is 3, assuming that the olive oil extracts at least 3 times more efficiently than cheese; for fatty meat (e.g. ham, salami, bacon) it is 4 (Directive 85/572/EEC). For simulant D and materials intended for contact with foods containing more than 20% fat, both FRF and DRF may be applied, being multiplied to give the total reduction factor (TRF). As proposed by the Super Regulation, the TRF may not exceed a value of 5. It is often around 5, because a high fat content tends to result in a high FRF but low

DRF, while for foods containing little more than 20% fat a negligible FRF is combined with a high DRF. EU legislation is generally interpreted as giving migration into food and food simulants the same weight (''food or food simulants''), leaving open which result prevails in case of a disagreement. It requires that migration be determined with simulants when no validated method of analysis is available for the food, but since for many compounds having an SML there is not even an official method for simulants, often other methods must be applied anyway. (Grob et al., & 2005).

A common complaint is that the present European legislative system for food contact materials includes exceedingly large safety margins. This is usually substantiated by the argument that nobody eats 1 kg of food contaminated with the substance under consideration at the SML every day, but neglects that for a majority of today_s packaged foods the migration limits apply per contact surface area and the maximum concentrations tolerated are often far higher. The present conversion of concentration limits to migration per contact surface area may cause the OM to exceed 1000 ppm and the TDI to be reached already with, e.g., 58 g sandwich cheese or sliced sausage. The introduction of the FRF will further reduce this amount. For small packs with a high surface area/volume ratio, the European system tolerates excessively high migration. The example of the PVC cling films shows that this problem is real. The European Commission is revising the plastic Directives by what is temporarily called ''Super Regulation''. As it introduces the FRF, this is the opportunity to revisit the rules on the conversion from concentration limits to limits referring to contact surface area. Considering the trend towards smaller packs, the present extreme relationship (cube of 6 dm^2/l) reflects reality ever less. Rather than lowering the threshold down to which the concentration limit is applied for containers (as proposed for the Super Regulation), the ratio of concentration in food to migration per contact surface area should be adjusted. The following changes are proposed

1. Migration limits be converted from concentrations in food or simulants to migration per contact surface area by a ratio of 20 dm^2/l.

2. Limits be in terms of concentrations in foods for ratios of contact surface area/volume up to 20 dm^2/l; abovethis ratio, migration is calculated per surface area. The same rules apply to fillable and non-fillable packages.
3. EU legislation clarifies that migration into foods prevails over migration into simulants. It no longer sanctions DRFs in situations where these are excessive. Conversely, data on migration into foods may be used to show compliance when migration is overestimated by simulation. (Grob et al, & 2005).

5.2.3.2 Execution of migration tests

After being set up in a migration cell, the unprinted side of the packaging is coated with the particular food simulant in question. After a specified exposure time at a defined temperature, the concentration of migrants in the foodstuff or simulant is measured (Huber Group, 2002).

Particularly in the case of folding boxes or paper packages, this method does not work because the materials are permeated by food simulants and extract substances originating from the printed image from the reverse side. The same happens if, for example, ethanol with a concentration >50 % is used as a fatty simulant for testing thin, printed polyolefin films (Huber Group, 2002).

In the case of cardboard packaging, Tenax is a suitable simulant for determining the transfer of non-polar migrants to fatty foodstuffs. Tenax is used in the form of a powder (grain size: 0.18–0.25 mm) and is a modified polyphenylene oxide (MPPO) (Huber Group, 2002).

5.3 Legal Frameworks About Migration

In order to protect consumers from the migration of harmful substances from packaging to foodstuff, CEC (Commission of the European Communities) Directives have been implemented for plastics packaging materials within the European Communities. The first relevant CEC Directive was issued in 1976 on the approximation of the laws of the Member States related to the subject Apart from harmonized legislation, the directives proposed analytical test methods to enable limits in the Directives to be respected. In 1980, the Commission Directive laid down the first Community method of analysis for the official control of vinyl chloride monomer level in food packaging materials. In general, the Directives introduced limits upon the overall migration from plastics into food and food simulants. In addition, specific migration limits or composition limits for free monomers in the final article have been set for some monomers. Currently, the limit for overall migration was set at 10 mg/dm or 60 mg/kg of food simulant. It also includes the lists of permitted monomers together with the restrictions which apply to specific monomers. (Lau & Wong, 2000).

In the USA, the structure of the regulations for food packaging material is much more complex. The regulations encompass both the basic polymer resins used in food packaging and the adjuvants, which are added to a polymer in the process of manufacturing the final food package. Regulations frequently contain specifications for the resin, such as residual monomer content. In addition, limits are sometimes placed on specific migration. More often, the regulations for polymeric resins limit global migration from the packaging. The time/temperature/solvent conditions for the short-term extraction tests used to test compliance are also spelled out in the regulation. Furthermore, in the Federal Register of 17 July 1995, the US Food and Drugs Administration (FDA) established a 'threshold of regulation' process. This process was proposed for determining when the extent of migration to food is trivial that safety concerns would be negligible. Based on this regulation, pre-market approval by FDA is currently required for food packaging materials to be used in the USA.

However, food packaging has not received much attention within the Codex Alimentarius Commission supported by the Food and Agriculture Organization of the United Nations and the World Health Organization. In the Codex Alimentarius, it specifies that packaging should not transmit to the food product substances beyond the limits acceptable to the official agency having jurisdiction. The Codex

Alimentarius contains guide-line levels for vinyl chloride monomer and acrylonitrile in food. (Lau & Wong, 2000)

Consumer Safety is an important guiding star for lawmakers in the EU. Therefore also food contact materials and articles are regulated. Packaging protects food from the environmental factors such as light and oxygen, and by that e.g. extends the preservation time and protects characteristics of food.

Harmonization of European regulations relating the principle of inertia of food contact materials (FCM) is quite recent and still under investigation since the general framework directive was published years ago. Current European Union (EU) regulation is based on the concept of a positive list that describes which monomers and additives are authorized and their conditions of use regarding a specific or global migration criterion into food articles. Moreover, EU regulation requires the manufacturer of a new substance or packaging to notify the appropriate authority and to carry out a risk assessment based on migration quantification, toxicity data (such as cytotoxicity, mutagenesis, estrogenic activity), and comparison with existing or proposed daily intake levels (Vitrac, & Hayert, 2005).

Basic principles for food contact materials and articles in European Union are laid down in the framework regulation 2004/1935/EC. This regulation shall apply to materials and articles, including active and intelligent food contact materials and articles, which in their finished state:

(a) are intended to be brought into contact with food; or
(b) are already brought into contact with food and are intended for that purpose; or
(c) can reasonably be expected to be brought into contact with food or to transfer their constituents to food under normal or foreseeable conditions of use.

The regulation shall not apply to antiques, covering or coating materials, which form part of the food and may be consumed together with this food or, fixed public or private water supply equipment.

The most important general requirements for all food contact materials and articles are laid down in Article 3.1 of the framework regulation

Article 3.1

Materials and articles, including active and intelligent materials and articles, shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could:

(a) endanger human health; or

(b) bring about an unacceptable change in the composition of the food; or

(c) bring about a deterioration in the organoleptic characteristics thereof.

The packaging should have no negative interaction with the food and should not change taste and odour of the food.

In addition to these general requirements more specific requirements are laid down for plastic materials and articles in Directive 2002/72/EC and amendments; 2004/1/EC and 2004/19/EC 2002/72/EC contains a list of monomers and other starting substances, which may be used in the manufacture of plastic materials or articles.

The plastic material is not totally inert and substances transfer from the plastic packaging into the food and vice versa. This transfer of substances is regulated by 2002/72 with two different migration limits i.e. overall migration limit and specific migration limit (SML). The overall migration limit, the total quantity of substances released by the sample, is 60 mg/kg or 10 mg/dm^2. Some substances are also regulated with SML, because toxicological data submitted to the Authority has been limited or its impact in higher transfer level has considered to be a concern. Specific migration limits are mentioned in Annex II of 2002/72/EC.

82/711/EEC2 (amendments 93/8/EEC and97/48/EC) and 85/572/EEC lay down the rules for verification of compliance with the migration limits. 82/711/EEC describes rules for migration testing and 85/572/EEC lists simulants to be used for each foodstuff or group of foodstuffs. It is also possible to use recognised diffusion models based on scientific evidence for the estimation of migration level of a substance. The commercial diffusion models don't give an exact value of migration, but they provide so-called 'Worst Case' migration scenarios, which ensure the protection of consumer safety (Polyolefins, 2005).

5.3.1 Packaging and Migration Legislations In Turkey

The first EU directive about the classification, packaging and labelling of dangerous chemicals was published in 1967 ın our country, after the foundation of "Ministry of Environment" one of the first regulations is the regulation for dangerous chemicals which was published in 1993 and adapted from EU regulations. According to this regulation, dangerous chemicals covers the substances and preparations which include one or more properties such as explosive, corrosive, flammable, hazardous, oxidizing, irritating, allergic, carcinogenic, mutagenic, toxic to reproduction and cotoxicologic.

Therefore, hundreds of chemicals used in several packaging industries can be defined as dangerous chemicals according to the regulation for dangerous chemicals and the necessary precautions should be taken account by the users (İkizoğlu, 2003).

Many laws and practices are determined with international guidelines such as GMP (Good Manufacturing Practices) or Food Codexes. Turkısh Food Codex come in to force in November 1997.

These are the communiques about migration test in printing.

Turkısh Food Codex, The Official Gazette 04.07.2005-25865

-Communication On Basic Rules Necessary For Testing Migration Of Constituents Of The Plastic Materials And Articles That Are In Contact With The Foodstuffs

-Communication No :2005/34 Communiqué on Plastic Materials and Articles that are in Contact with the Foodstuffs

-Communication No :2005/31 Communiqué on Epoxy Derivates Materials and Articles that are in Contact with the Foodstuffs

-Communication No :2005/32 Communiqué on List of Simulants to be used for Testing Migration of Constituents of the Plastic Materials and Articles that are in Contact with the Foodstuffs

-Communication No :2005/33 Communiqué on Materials and Articles in Contact with Foodstuffs

-Authorization Law: Turkish Food Codex The Official Gazette: 22.04.2002-24734, Communication No : 2002/32

5.3.2 Adaptation of Turkish Packaging Industry to EU

Mainly packaging directives of EU and Turkey are given in table:

Table 5.1 Mainly packaging directives of EU and Turkey (Yiğit, 1999)

EU	Turkey
Eu directives	Turkish legislations
Filling capacity and standartds	Turkish standardisation and regulations of measures
Surfaces of Coming in to contact with food	Turkish Food Codex
Ecological labelling	Regulation on controling of dangerous chemical substances.
Marking	-
Package and wastes	Regulatin on controlling of solid wastes

5.4 Good Manufacturing Practice of the Packaging Printer

The six recomendations listed for printers of food ad pharmaceutical packaging are taken from a publication of the SICPA group:

*no direct contact between the printed ink and the food.

The printer should ensure that no direct ontact canoccur between the printed surface and food at any point of the packaging.

*there must be a functional barrier

The printer should ensure the presence of an effective barrier between the ink film and the food (eg. Suitable film or alluminum foil)

*minimization of migration by the selection of the right printing

Migrating materials from the printing inks may possibly deposit themselves on the inside, and can subsequently comeinto direct contact with the food.

*requirements on the packaged products and on use by the customer.

The printer is required to take in account not only the sbstrate, the printing ink and the printing method, but also the further processing up to the finished packaging by the consumer. If packaging is printed which is to be sterilized together with the packaged product or which is heated up by the consumer in a bakig/microwaveowen the printeris advised to use printing inkswith the appropriate specifications. This also applied for packaging of fats meat, ready cooked meals, fruit juices and like. Such packaged products have a high extraction potential, meaning that they literally promote diffusion and mixing with migratory substances.

*check of drying and curing.

The printer should ensure that the printing ink is as solvent free as possible or that UV and ofset inks have completely cured according to the standards adopted for use in the respective branch.

*due diligence of the printer to provide information

The printer shoul regard it as his due dilligence to obtain the pertinent informartion from the packaging manufacturer., respectively from the end user relating to the purpose for which the packaging is intendence and how it is used. The objective has to be not only the technical quality but also the migratory inertness of the packaging up to the consumer (Sandro, 2003).

CHAPTER SIX
EXPERİMENTAL STUDY

6.1 Experimental Study

In order to compare the migration properties of isopropyl alcohol and butyl acetate which are in use with n-heptane, migration tests have been performed by Public Health Center of Ministry of Health. UV cationic lacquer series prepared by n-heptane have been applied to dry/wet offset, metal offset, packing material surface and wooden furniture. The packing material has been sent to Public Health Center for migration test.where very low migration is anticipated, such as for inorganic adjuvants or certain highly cross-linked polymers, heptane can be usefuldue to the ease of of analytical work group, therefore although heptane migration data may continue to be accepted, migration values will not be divided by any factor unless there is adequate justification. The results of the migration test are given in Table 6.1 and 6.2.

Table 6.1 Migration Properties of UV Cationic lacquer applied to polyester folio material.

Analyzed parameters	Result (mg/dm^2)	Turkish Food Codex limit (mg/dm^2)	Method
Pure water migration (40^0C, 2 days)	1.6	10	Migration
Pure water migration (40^0C, 5 days)	2.8	10	Migration
Pure water migrations(40^0C, 10 days	2.8	10	Migration
Pure water migration (70^0C, 2 hours)	0.95	10	Migration
n-heptane migration (70^0C, 2 hours)	0.37	10	Migration
n-heptane migration (21^0C, 30 min)	0.3	10	Migration

Table 6.2 Migration Properties of UV Cationic lacquer applied to tin plate.

Analyzed parameters	Result (mg/dm^2)	Turkish Food Codex limit (mg/dm^2)	Method
n-heptane migration (70^{0}C, 2 hours)	0.53	10	Migration
Pure water migration (40^{0}C, 2 days)	5.44	10	Migration

As can be seen from Table 6.1 and 6.2, migration values are much lower than the limit set by Turkish authorities. Since these UV-Cationic lacquers have very low migration, the next step is to use these preparations in the market. Although the cost of the formulations is somewhat higher than equivalents, lower migration and health hazards make On 13 November 2004 the new Framework Regulation on materials and articles intended for food contact was published in the Official Journal.

CHAPTER SEVEN
CONCLUSION

An estimation of one thousand new chemicals enter the market every year, and about 100000 chemical substances are used on a global scale. These chemicals are mostly found as mixtures in commercial products. One to two million such products or trade names are available.

Many specific chemicals in widespread use are hazardous for living organisms, materials, structures, or the environment because of their chemical reactivities, fire hazards, corrosivities, toxicities, and other characteristics.

In printing, many chemicals are used in inks, additives, cleaning products, etc. Solvents have VOC's (volatile organic compounds) which has hazardous characteristics, so they pose a serious risk for human and environmental health and safety. Some chemicals used in printing are in 'Highly Hazardous Chemical, Toxic and Reactive List' such as; acetaldehyde, ammonia, ethylamine, formaldehyde and hydrogen chloride, or in priority pollutant list such as benzene, methylene chloride, toluene, tetrachloroetylene, trichloroethylene and cadmium, chromium and copper compounds.

Many universities and companies have studied and investigated about health problems in printing industry. For instance solvents have VOC's and they could affect hormonal regulation or increase early fetal losses which in turn contributes to longer times of unprotected intercourse. Other chemical toluene used in printing is also hazardous and increasings of toluene rates in blood were seen in worker's blood system. And the slow decrease of toluene in venous blood was followed for two weeks after cessation of exposure. As we can see that there is a clear relationship between hazardous chemicals used in printing and illnesses. It is undeniable realism.

Hazardous chemicals uses are limited with directives, especially European Union's (EU) directives try to limit hazardous chemical.

European Union (EU) has regulated many directives and standards about minimization of hazardous chemicals used in industries. Some of them are given below:

a)67/548/EU (Classification and Labeling of Dangerous Substances Directive)
b)88/379/EU (Classification and Labeling of Dangerous Substances Preparation Directive)
c)93/112/EU (EU Safety Data Sheet Directive)
d)76/769/EEC (Dangerous substances and preparations legislation)

For some years a number of National Association members of European Council of Paint, Printing Ink and Artist Colors Industry (CEPE) have been independently composing voluntary recommendations for the exclusion of certain raw materials (substances and preparations according to the definition given in the Dangerous Substances Directive 67/548/EU) from printing inks and related products. These exclusion lists of materials have been based on health and safety matters in the day-to-day production and marketing of printing inks and associated products employing Good Manufacturing Practices.

In Turkey with the 6th of the November in 2001 chronogram and 24575 numbered decision in formal newspaper, "Hazardous Chemicals Regulation" was publicated. And 4th item of this regulation includes some chemical properties used in Printing and Package Industry:

1-Flammable substances 2-Highly toxic substances 3-Harmful substances 4-Corrosive substances 5-Irritative substances 6-Allergic substances 7-Carcinogenic substances 8-Mutagen substances 9-Heavy metal pigments and fillings

Nowadays there are innovations in printing like other sectors, and UV printing, UV cured inks and even UV cationic inks and lacquers have been developed. The implementation of the 1990 Clean Air Act (CAA) has had a major effect on the coatings industry in terms of reducing Volatile Organic Compounds (VOCs).

Ultraviolet (UV) curing coatings have emerged as one of the efficient vehicles to challenge the VOC limits in organic coatings. In addition, UV coatings also offer the advantages of fast curing speed, high energy efficiency, and low capital investment and space requirement. These coatings are especially suitable for the wood (furniture) or plastics coating, metal decorating, and paper printing industries. This is a consequence of an ambient temperature cure. There are two principle mechanisms in which the UV coatings polymerize on the substrates, free radical and cationic. The most widely used in UV-radiation curing: acrylates, which polymerize by a radical mechanism, and epoxides, which polymerize by a cationic mechanism.

Although UV light drying technologies have already been in use for over 30 years in the printing industry, it is still considered as a new technology in comparison with conventional printing. Before UV-curing technologies, hazardous chemicals containing VOC's and heavy metal pigments are used in printing, causing health problems on workers. Furthermore for 30 years chemical substances such as benzophenols, amines and acryclic acids have been used in conventional UV curing and these were also harmful for the people and environment.

Although there is a number of niche alternative curing technologies, by far the most important is cationic curing. After 1999/45/EEC, European Union countries have started research and development to reduce the human exposure to hazardous chemicals. From these studies reactive UV-Cationic inks and lacquers were formulated with properties of nearly zero migration rates and no VOC content. EU directives propose these UV-Cationic inks and lacquers. These cationic UV printing ink and lacquers and chemicals also have less hazardous properties. In terms of their use in food packaging applications, cationic curing inks are desirable because, in theory at least, the post-cure reaction will continue until all the monomer is consumed, thus minimising migration. A further significant advantage is the superior mechanical properties of cationic inks and coatings following post cure, allowing them to survive processes such as steam sterilisation and retorting which are becoming increasingly important in the food packaging sector. These advantages are countered by the cost, slow cure speed, weak inks, high odour on cure and humidity inhibition to the extent that their use is often too much of a compromise, particularly when competing against an established technology like free-radical.

The substances that may migrate and that may affect the safety of the food obviously depend on the nature of the packaging material. The constant introduction of novel packaging materials has increased the number of specific hazards to which humans are exposed via the migration from packaging into food.

The concentration of the migrants in the packaged food depends on:

• the initial concentration of the migrant in the printed packaging
• the speed with which the migrant migrates (diffusion speed)
• the equilibrium of distribution of the migrant, that is, its solubility in the printed packaging and in the foodstuff.

And also heat, contact time, food characteristics (oily, dilute, watery or acidic forms), mass state of foods (grain, powder, liquid, or paste state), physical and chemical cahracteristics of printing and packaging materials, concerns of products element to migrants or amount of materials that ready to migration are other important factors about migration speed and size

In order to compare the migration properties of isopropyl alcohol and butyl acetate which are in use with n-heptane, migration tests have been performed by Public Health Center of Ministry of Health. UV cationic lacquer series prepared by n-heptane have been applied to dry/wet offset, metal offset, packing material surface and wooden furniture. The packing material has been sent to Public Health Center for migration test.

As can be seen from results migration values are much lower than the limit set by Turkish authorities. Since these UV-Cationic lacquers have very low migration, the next step is to use these preparations in the market. Although the cost of the formulations is somewhat higher than equivalents, lower migration and health hazards make On 13 November 2004 the new Framework Regulation on materials and articles intended for food contact was published in the Official Journal

Recommendations can be given to protect workers health in printing sector. Some recommendations for the printing sector are given below;

- Use safer solvents than the others
- Use solvent that can evaporate hardly instead of easily ones
- Pay attention with spilling, dropping, and prevent the direct touch with solvents
- Good ventilation systems
- Change process - for example use safer UV- cationic ink and lacquers
- Use low migrated chemicals
- Decide what control measures are needed, and how to provide them
- Maintain all control measures and ensure they are used
- Monitor exposure levels and provide health surveillance, as required
- Provide employees (and others) with necessary information, instruction and training
- Minimize the organic pigment amounts that are used in primary school lesson book
- Use biodegradable resins

We can take some prevetive measures like substitution, engineering control, safe working procedures (code of practices), reducing exposure, personel protective equipments, monitoring, hazard communication (Labelling and MSDS), training .

In Turkey, there is a big development in legal framework and its applications on occupational health and safety. Therefore many changes in working conditions in printing sector (as well as other sectors) are expected in the near future.

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