

Chemicals: Interactions in Art, Humans and Nature by ECKHARD STROEFER-HUA

"Everything in excess is a poison and only the dose makes a thing not being a poison." Each responsible handling of chemicals is based on that deep wisdom of Paracelsus.¹ Remedies must be given in the proper dose. Too high a dose is harmful. Poisons given in the right quantity may have a curative effect. Chemicals used in restoration may protect a piece of art and support its beauty. A bleaching agent applied at an excessive concentration destroys the object to be saved. The book by Waechter² contains many such empirical recipes. The problem for the restorer is not just to find the right recipe qualitatively but to find the right quantitative dose in practice.

All inorganic and organic nature is based on chemical compounds. Inorganic salts, sugars, amino acids etc. belong to the myriad of compounds from which the structures of our world are formed. In these structures, the various chemical compounds interact in properly dosed amounts and thus enable evolution and life.

Catalysts and chemical messengers in our body such as enzymes and hormones only function well if they are present at the right concentration. Inappropriate concentrations of insulin disturb people's metabolism. Calcium, magnesium, copper, iron, chromium, manganese, zinc and cobalt are minor elements that are essential for life. However, in a test with animals, 80 mg of cobalt chloride per kg body weight kills one half of the test animals (LD 50). Compounds with an LD 50 larger than 2 g per kg body weight are not defined as being poisonous any more.

Restorers are familiar with salts of heavy metals as parts of colour pigments. For deacidification of papers they use salts of earth alkaline elements. Restorers even work with enzymes in case they want to destroy animal glues. Restorers use a broad range of inorganic and organic chemicals.

CYCLES OF MATTER

Chemistry is everywhere. The complex interactions between different compounds with the effect depending on the dose determine the living spaces and the cycles of matter in these living spaces.³⁻⁶ Fig. 1 gives an example: the paper cycle of which the restorer is a part. Each year huge amounts of energy and carbon are recycled in the biosphere. Such compounds as starch, cellulose, hemicellulose and lignin are formed by plants from simple molecules like water and carbon dioxide under the influence of sunlight. Starch may be decomposed to sugar and is used as a foodstuff or a raw material in the chemical industry.⁵ In a modified form, starch is used directly as an auxiliary material in the fabrication of paper.⁷

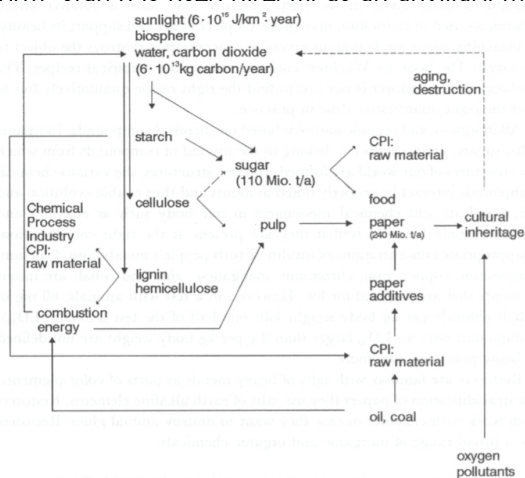


Fig. 1. The paper cycle

Paper is the main carrier of cultural evolution, as was demonstrated by the development of the Chinese culture.^{8,9} Cellulose is mainly used for paper production. Of course not the whole world production - 240 million tons in 1990 - is used for written culture. The production of cellulose generates equivalent amounts

of hemicellulose and lignin.⁴ Wood processing requires energy, as does life. Usually the energy is produced by combustion of oil or coal. Hemicellulose and lignin were previously discharged as wastewater and polluted the rivers. Nowadays they are burnt, too, and energy is gained. The main products of combustion are again carbon dioxide and water, which are recycled into the biospheric cycle.

Oil and coal are the basic raw materials for the chemical industry. They are used to produce such paper auxiliaries as polyacrylamide, formaldehyde, resins, polyethylenimine, pigments and dyes.⁷

The various chemical compounds of paper are attacked by oxidizing substances or air pollutants. Different papers age in different ways, depending on the storage conditions, air or internal pollutants and mechanical and other stress that might attack the paper differently. Air pollutants include sulfur dioxide, nitrogen oxides and tropospheric ozone,¹⁰ which are byproducts of combustion processes. An example of an internal pollutant is aluminum sulphate.¹¹ Finally, paper decomposes again to carbon dioxide and water.

The restorer tries to influence the process of aging of paper, again using such chemicals or bleaching agents that can be poisonous or corrosive; they might be gases or liquids that can be inflammable, corrosive or poisonous; they might be pigments and dyes that might also be poisonous or corrosive.

What are the effects on the cycles of nature of the chemical compounds mentioned above with respect to their recycling?

CHEMICALS IN DIFFERENT ENVIRONMENTS

The industrial production of energy from oil and coal results in an additional release of carbon dioxide into the atmosphere. Since 1850 the concentration of carbon dioxide has increased from about 280 ppm to 350 ppm. Computer simulation predicts an increased temperature in the Earth's atmosphere: the greenhouse effect. It may influence the climate⁶ and herewith the preservation of cultural property and the restorer's work.

Paper is not only used as a carrier of cultural property. Huge amounts are present as waste and garbage left from other use, such as packaging and hygiene. This leads to problems of recycling, multiple use or deposition. The restorer knows well the problems of de-inking and the typical properties of recycled paper. Hemicellulose and lignin from paper production are a mixture of natural substances. High concentrations of them in the wastewater of paper factories disturb ecological systems.

Table 1. The ideas of Bruce N. Ames¹³

Common sense suggests that a chemical pollutant should not be treated as a significant hazard if its possible hazard level is far below that of common food items. TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) is a substance of great public concern because it is an extremely potent carcinogen and teratogen in rodents, yet the doses humans are exposed to are very low relative to the effective level in rodents. Let me analyze the dioxin question in some detail below to illustrate this point. We can compare TCDD to alcohol as an example. Alcohol is an extremely weak carcinogen and teratogen, yet humans are exposed to high dose relative to the effective dose in rodents (or humans). Indeed, alcoholic beverages are the most important known human teratogen, and the effective

(5 drinks/day) dose level of alcohol in humans in mg/kg is similar to the level causing birth defects in mice. By contrast, there is no convincing evidence that TCDD is carcinogenic or teratogenic in man, although it is in rodents. If the teratogenic potential of TCDD is compared to that of alcohol for causing birth defects, after adjusting for their potency in rodents, then a daily consumption of the EPA reference dose (formerly, acceptable dose limit) of TCDD, 6 fg/kg/day, is equivalent in teratogenic potential to the amount of alcohol ingested daily from 1/3,000,000 of a beer, the equivalent of drinking one beer (15 g ethyl alcohol) over a period of 8,000 years. A daily slice of bread or a glass of orange juice contains much more natural alcohol than this.

Therefore, it seems likely that a high percentage of all of the chemicals in the world, both manmade and natural, will be classified as carcinogens. Most of these, however, may not be of interest at doses much below the toxic dose.

Modern technologies are always replacing older, more hazardous technologies. The reason that billions of pounds of the solvents trichloroethylene (TCE, one of the most important industrial nonflammable solvents) and perchloroethylene (PCE, the main dry-cleaning solvent in the U.S.) are used is because of their low toxicity and the fact that they are not flammable. Is it advisable to go back to the age when industry or dry cleaners used flammable solvents and frequently went up in flames? Eliminating a carcinogen may not always be a good idea. For example, ethylene dibromide, the main fumigant in the United States before it was banned, was present in trivial amounts in our food. The average daily intake was about one-tenth of

the possible carcinogenic hazard of the aflatoxin in the average peanut butter sandwich, a trivial risk in itself. Elimination of fumigation results in insect infestation and subsequent contamination of grain by carcinogen-producing molds. This might result in a regression in public health - not an advance - and would also greatly increase costs. The coming alternatives, such as irradiating food, could be more hazardous than ethylene dibromide as well as more expensive. Similarly, modern pesticides replaced more hazardous substances such as lead arsenate, one of the major pesticides before the modern era. Lead and arsenic are natural, highly toxic, and carcinogenic. Pesticides have increased crop yields and brought down the price of foods, a major public health advance.

Americans ingest in their diet at least 10,000 times more by weight of natural pesticides than of man-made pesticide residues. These natural toxic chemicals have an enormous variety of chemical structures and appear to be present in all plants, in which they serve as protection against fungi, insects, and animal predators. Although only a few dozen are found in each plant species, natural pesticides commonly make up 5-10% of the plant's dry weight. There has been relatively little interest in the toxicology or carcinogenicity of these compounds until quite recently, although they are by far the main source of toxic chemicals ingested by humans.

Most chemicals tested for carcinogenicity in rodent bioassays are synthetic compounds; however, the proportion of positive tests is about as high for natural pesticides as for synthetic chemicals (roughly half). Because more than 99.99% of the pesticides we ingest are nature's pesticides, our diet is likely to be high in natural carcinogens. Their concentration by weight is usually in parts per thousand or more, whereas that of synthetic pesticide residues of water pollutants is usually in parts per billion. The known natural carcinogens in anise, apples, bananas, basil, broccoli, Brussels sprouts, cabbage, cantaloupe, carrots, cauliflower, celery, cinnamon, cloves, cocoa, comfrey tea, fennel, grapefruit juice, honeydew melon, horseradish, kale, mushrooms, mustard, nutmeg, orange juice, parsley, parsnips, peaches, black pepper, pineapples, radishes, raspberries, tarragon, and turnips are undoubtedly just the beginning of the list of natural carcinogens, because so few of nature's pesticides have been tested...

The idea that nature is benign and that evolution has allowed us to cope with the toxic chemicals in the natural world is not compelling, for several reasons:

° There is no reason to think that natural selection should eliminate the hazard of carcinogenicity of a plant toxin that causes cancer past the reproductive age. For example, aflatoxin, a mold toxin that presumably arose early in evolution, causes cancer in trout, rats, mice, and monkeys - and probably people - although the species are not equally sensitive. Many of the common metal salts such as lead, cadmium, beryllium, nickel, chromium, selenium, and arsenic are carcinogens despite their presence during all of evolution.

° It is argued by some that humans, as opposed to rats or mice, may have developed resistance to each specific plant toxin or chemical in cooked food. This is unlikely, because both rodents and humans have developed many types of general defenses against the large amounts and enormous variety of toxic chemicals in plants (i.e. nature's pesticides). These defenses include the constant shedding of the surface layer of cells of the digestive system.

° The human diet has changed drastically in the last few thousand years, and most of us are eating recently introduced plants - such as coffee, potatoes, tomatoes, and kiwifruit - that our ancestors did not.

Combustion of coal, oil, lignin, paper etc. forms certain byproducts classified as air pollutants. They may interact with cultural property. Nitrogen oxides are natural byproducts in the metabolism of bacteria in the soil. However, they are locally released in high concentrations by combustion processes, especially from exhaust gases by vehicular traffic, and they act as air pollutants.

The legal limit for long-term exposure for the general public is about $0.2\text{mg}/\text{m}^3$. At workplaces where normally only healthy adults are working, a maximum of $10\text{mg}/\text{m}^3$ is tolerated (the MAK value = maximale Arbeitsplatz-Konzentration

= maximum concentration at the workplace based on the relevant laws in

Germany).¹² From nitrogen oxides and hydrocarbons, be they of natural or human origin, ozone can be formed in the atmosphere. This tropospheric ozone must not be confused with the stratospheric ozone (the ozone layer that protects the Earth from harmful radiation). Ozone, as a strongly oxidizing agent, acts on people, flora, fauna, and cultural assets.

It does not make sense to separate human-made chemical compounds from natural ones and to play off nature against industry. Both are chemistry. Nitrogen oxide, ozone and carbon dioxide are natural substances; their effects on humans and the environment depend on the dose or the concentration in the atmosphere and not on their origin. The increase of carbon dioxide in the atmosphere spurred scientists to predict the greenhouse effect. At a workplace, however, 350 ppm (690 mg/m³ air) is neither poisonous nor harmful. The MAK (see above) is

9000 mg/m³. If the amount of oxygen decreases from 21% in air to less than 17% by dilution with carbon dioxide, human beings die from suffocation.

Table 1 presents some ideas of Bruce Ames pertaining to the struggle of so-called natural versus human-made substances.^{13,14} There is no reason to hysterically reject such human-made substances as pesticides. In the same way that there is no reason to propagate so-called natural restoration, using only chemicals of natural origin and avoiding all industrial products. We have more experience on the long-term behavior and use of such products as starch and gelatin, which have been known for centuries, than of modern synthetics. But this is a different problem. The long-term abiding behavior of many modern compounds is not sufficiently known because not enough creative energy has been focused on that problem.¹⁵

Ames' main interest is chemicals that are poisonous or carcinogenic for human beings. Huge numbers of possible chemical compounds fit these criteria, and evolution has learned to handle them. In general, human-made substances are accepted to have a higher carcinogenic potential than natural ones. But this is only true because, until now, natural substances have been examined for their carcinogenic potential less frequently than human-made ones. For all substances, the human-made and the natural ones, the effect on people and the environment depends on the dose, the way of application, the intensity and the time of interaction.

Humans have produced about 7 million chemical compounds in the laboratory; industry produces 100,000 of these. The number of natural compounds is larger by several orders of magnitude. May the artificial compounds be called bad and the natural ones good? Of course not.¹⁶ Pharmaceutical substances, fungicides, pesticides, chemicals for industry and reagents for the laboratory have a good or bad effect depending on the dose or the concentration of application.

Restorers use fungicide to get rid of mold in paper. The dose is important; if the concentration is too low, the mold is not killed. If the concentration is too high, the paper can be damaged, depending on the properties of the fungicide (oxidation potential and pH value).

CHEMICALS IN THE WORKSHOP

Last but not least, restorers have to protect themselves against the adverse effects of chemical compounds. Small amounts of certain substances may be poisonous. In what way can these substances penetrate the human body? This may happen by swallowing them, for example, during eating at work if the substance is present. Gases or vapors penetrate via the lungs by breathing; liquids may penetrate through the skin when they are touched by a hand not wearing a glove.

Finally, the waste resting in the restorer's workshop after a damaged sheet is treated with the fungicide has to be disposed of properly to prevent pollution. The same is true for any other chemical compound. Bleaching agents, too, have to be used at a proper dose to prevent side effects and to result in the desired effects. Restorers working with bleaching agents have to protect themselves. The dose that may just be the right one for a specific restoration can harm the health of the restorer. A splash of hypochlorite solution into the eye will result in heavy cauterization. The restorer therefore has to wear safety goggles. The best and, to be honest, the only proper discharge of waste after bleaching is done by preventing it in the first place: prepare as little as possible of the bleaching agent; as little as is really needed for the sheets to be bleached.

The restorer handles natural and human-made chemical compounds. Turpentine is a mixture of flammable hydrocarbons. Eau de Javelle is hypochlorite, which may cause cauterization. Lead white contains the poisonous metal lead. The dose and the concentration that are good for the object to be restored can be harmful and dangerous for restorers and their environment. How can restorers be protected?

I hope that this article will encourage restorers to study intensively the guidelines 12,17-23 on the use of hazardous chemicals and on the use of chemicals in general at the workplace. Because of their education, restorers should be able to understand tables with data on hazards caused by chemicals and to use the relevant measures of protection. Articles in the technical literature may be helpful for this.²⁴⁻²⁷ The chief restorer of a workshop is responsible for his or her colleagues. The substance of this responsibility is that

she or he is obliged legally to enforce the relevant safety and protection guidelines, such as safety goggles, safety gloves and no food at the workplace. As far as possible, chief restorers must prevent people from handling carcinogenic chemicals and prevent pregnant women from working with teratogenic substances. Moreover, chief restorers are responsible for the correct safety classification of bottles and containers. They are responsible for the cleanliness of the workplace.

Table 2. Symbols of hazardous substances










 <p>E: Spanish: explosivo Danish: eksplosiv German: explosionsgefährlich Greek: εκρηκτικό English: explosive French: explosif Italian: esplosivo Dutch: ontplofbaar Portuguese: explosivo</p>	 <p>O: Spanish: comburente Danish: brandfarende (oxiderende) German: brandfördernd Greek: εύφλεκτο English: oxidizing French: comburant Italian: comburente Dutch: oxyderend Portuguese: comburente</p>
 <p>F: Spanish: fácilmente inflamable Danish: let antændelig German: leichtentzündlich Greek: εύφλεκτο English: highly flammable French: facilement inflammable Italian: altamente infiammabile Dutch: gemakkelijk ontvlambaar Portuguese: facilmente inflamável</p>	 <p>F+: Spanish: Extremadamente inflamable Danish: yderst let antændelig German: hochentzündlich Greek: εύφλεκτο English: extremely flammable French: extrêmement inflammable Italian: estremamente infiammabile Dutch: zeer licht ontvlambaar Portuguese: extremamente inflamável</p>
 <p>T: Spanish: tóxico Danish: giftig German: giftig Greek: τοξικό English: toxic French: toxique Italian: tossico Dutch: vergiftig Portuguese: tóxico</p>	 <p>T+: Spanish: muy tóxico Danish: meget giftig German: sehr giftig Greek: πολύ τοξικό English: very toxic French: très toxique Italian: molto tossico Dutch: zeer vergiftig Portuguese: muito tóxico</p>
 <p>C: Spanish: corrosivo Danish: ætsende German: ätzend Greek: διαβρωτικό English: corrosive French: corrosif Italian: corrosivo Dutch: corrosief Portuguese: corrosivo</p>	
 <p>Xn: Spanish: nocivo Danish: sundhedsfarlig German: mäßiggiftig Greek: επιβλαβής English: harmful French: nocif Italian: nocivo Dutch: schadelijk Portuguese: nocivo</p>	 <p>Xi: Spanish: irritante Danish: lokalirriterende German: reizend Greek: ερεθιστικό English: irritant French: irritant Italian: irritante Dutch: irriterend Portuguese: irritante</p>

Table 2 Symbols of hazardous substances

This is not the place to discuss the safety classification of hazardous chemicals in detail. Table 2 shows the symbols that characterize hazardous substances. The symbols, classifications and boundary limits given in this article and the tables may be slightly different in different countries and may be subject to changes with time. The relevant data must be verified in the literature given above.

POISONOUS CHEMICALS

About 4000 people die from poisoning each year in the United States. Half of these are children. In Great Britain approximately 100,000 poisonings per year were registered; 3000 resulted in death. These statistics estimate the risk for certain groups of population or for professional groups. For this purpose, quantitative methods to determine the degree of toxicity of a certain compound or a certain preparation have been developed. They are the basis for laws, legal guidelines and ordinances on handling toxic substances. In Germany one of them is the MAK. They guarantee that a human being exposed to the compound for 8 h per day and 5 days per week will not suffer adverse health effects. The MAK pertain to air pollution: they give the maximum allowable concentration of the substance in the air at a workplace. Limitations in the air for the general public, including children, old and sick people are, of course, much lower. This is true, for example, for smog-relevant substances (as one sees above). Restorers do not work daily with the same compounds in intensive contact as the professionals in the chemical industry do. MAK only provides an orientation.

If a new recipe is being tested for the first time (such as those by Waechter²) and the air in the workshop exceeds a relevant MAK, the restorer should feel alarmed. Restorers do not normally have the means for air analysis at their workplace, a routine in the chemical industry. Using a simplified method and finding a certain MAK exceeded for a short period of time, the restorer must not consider it a catastrophe. But this should be taken as a warning about when to stop the experiment. The restorer is not a chemist. The task is to restore cultural property for a long, long time, and doing so, restorers must avoid any risk for the object treated and to potential damage.

And another remark on risk. The chemical industry of Great Britain has compared the risk of health and death at its workplaces with the same risk the workers have in commuting every day and thus participating in street traffic. The latter risk was found to be much higher.

Acute toxicity and chronic toxicity must be distinguished. Acute toxicity means that health is affected within a short period of time. The measure of acute toxicity is described by the LD50. In the relevant tests with rats, irritating and corrosive properties are examined, too. To learn something about the chronic toxicity of a

compound, lifelong tests (about 2 years for rodents) with different doses are necessary. These lifelong tests also examine the formation of cancer. Ames has done important work in this field.

Carcinogenic substances act directly on the genomes of the cells or on the enzymes that catalyze genome copying and repair. The cell loses control of its rate of division and a tumor develops. The original events, such as the contact with a chemical and the formation of the tumor, may be several decades apart. This is why cancer becomes one of the major diseases when life expectancy rises in the industrialized countries. Examples of carcinogenic chemicals include aflatoxin produced by the fungus *Aspergillus flavus*, benzene and carbon tetrachloride.

Teratogenic substances may deform the fetus during pregnancy. The most famous teratogenic substance is the tranquilizer thalidomide, which was in the headlines in the 1960s. The expression teratogenic goes back to the Greek *teras*, which means unpromising signs of heaven, nightmare or monster. During pregnancy a woman should be very careful in handling such substances as benzene, xylol, carbon tetrachloride, chloroform, lead and alcohol (ethyl alcohol), including drinking alcoholic beverages.

Allergenic substances set off the immune system for people who are correspondingly sensitized. The most important substances that may initiate allergies are pollen and dust in general, perfumes, heavy metals (like those in pigments), tar from wood, rosin, rubber chemicals and formaldehyde. Formaldehyde is a frequently used preservation agent for glues and is used for disinfection. Rosin, the component of resin from pine trees, is used in varnish and sizing agents. Further literature to the wide field of toxicology is given in the references.^{17,28,29}

FIRE AND EXPLOSIONS

It is a bad habit in the restorer's workshop to use the label of the detonating bomb on bottles with inflammable organic liquids. The correct label is the flame symbol. The bomb is reserved for explosives. An area conflagration, as impressive as it might be, is not a detonation of trinitrotoluene (TNT).

All liquid organic solvents have a vapour phase above them in which the solvent's vapour is mixed with air. This gaseous mixture can be ignited by an electrical spark, an open flame or an electrostatic discharge. The speed of flame propagation is about 1 m/s, which is much too fast for people to react. The fire results in an explosion with great mechanical damage. During an explosion, the container that contains the solvent is usually destroyed. An area conflagration results.

Restorers should store the minimum amount of chemicals necessary in workshops. The total of inflammable solvents should never exceed 5 liters. If more solvent is needed, the portion for one working day should be filled up outside and the main portion stored in a separate room. Smoking is forbidden. Smoke damages the object to be restored, too.

All the chemical compounds mentioned somewhere by Waechter² do not have to be present in the workshop. Sovereign restorers work pragmatically. They have their standard recipes and if they need a special product they get it from the dealer at the time it is needed. The dealer handles the safety data sheets, too.³⁰ Chemicals that spoil after being stored for years only lead to waste and pollution problems, which result in a lot of work for the restorer and are a burden to the environment.³¹

Store different classes of chemicals separately. Acids and bases, solvents, oxidation and reduction agents, tools and pieces of arts may react with each other if the protective outer shield of the container is destroyed. This may be demonstrated: a hammer falls down from a shelf. It destroys a glass bottle with solvents in it. A spark from the electrical motor of a hair dryer ignites the mixture of vapor and air. There is a fire. The piece of art starts burning and the plastic bottle with hypochlorite solution is destroyed. The hypochlorite solution rinses the handle of the fire extinguisher. And the frightened restorer, who is hurt by corrosives and burns, is brought to hospital. Still more safety advice: each workshop must have enough ways to escape. The workshop must be separated from other housing and installations by a fireproof wall and self-closing doors. The workplace must have tested fire extinguishers that may be filled with water or carbon dioxide. Fire extinguishers that use powder may heavily damage the workshop and the pieces of art. It is recommended that the workshop have a main electrical circuit breaker, so that in the evening all installations can be switched off from a central point when leaving the workshop. Such simple protective measures can even be realized in small and medium-sized workshops.³²

GASEOUS SUBSTANCES

Ozone is used as an oxidizing bleaching agent. The MAK is about 0.2 mg/m³. In the atmosphere (see above: photochemical smog), the concentration of ozone should not exceed 120 ug/m³ for an 8-h average for protection of humans. For protection of the flora, a guideline of the European Community even proposes

70 ug/m³ for 8 h on average. Hypochlorite is chlorine dissolved in sodium hydroxide solution in water. In acidification of the solution, the chlorine escapes as a gaseous compound. In general, however, the maximum workplace concentration of

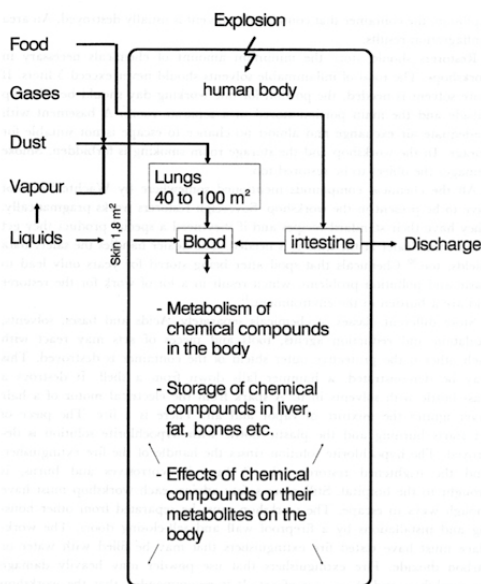


Fig. 2. Action of chemicals on and in the human body

1.5 mg/m³ is not exceeded if the air exchange in the workshop is good. For the hypochlorite solution, the important safety point is the corrosive character of the liquid. So especially splashing into the eyes has to be prevented and is dangerous.

Suffocation is a special danger if the proportion of oxygen in the air decreases from 21% to below 17% (in volume). Working with carbon dioxide (preparing solutions for deacidification) or nitrogen (killing insects) in rooms with no air exchange presents this danger.

Ethylene oxide is used for sterilization in hospitals and for disinfection of moldy books. This gas produces the danger of handling a substance classified as carcinogenic that may form explosive mixtures with air, in contrast to carbon dioxide and nitrogen. The only people who may handle ethylene oxide have special training in handling this substance and the corresponding equipment. I believe that restorers should not apply ethylene oxide in the workshop. If in extreme cases a treatment with ethylene oxide is really necessary, you can probably find a hospital to do the work for you.

MAK are partly given in parts of millions of the volume of the gas (ppm or ml/m³) of air. For conversion, the knowledge of the molecular weight of the special compounds in grams/mole is necessary.

LIQUIDS AND SOLIDS

The large group of organic solvents is of overwhelming importance for restorers. The MAK vary over several orders of magnitude. The good solubility of solvents in fat results in accumulation in tissues that are rich in fat and in the nerve system after the solvent penetrates the organism. This produces the narcotic effects that are common to all organic solvents. In general, however, the solvent only acts as a poison to the organism after a metabolic reaction in the body to the final toxic substances. Mainly the liver and the kidney may be damaged. Typical examples are benzene or carbon tetrachloride, which restorers should not use. Even gasoline contains some proportion of benzene. Very often the special problems of restoration may be solved by using heptane or methyl acetate. Excluding the problem of swallowing a compound, solvents can be inhaled or may be absorbed by the skin. This special lipophilic property of the solvents damages the skin. The protective layers of the skin can be destroyed to the extent that bacteria and spores may penetrate and favor the development of infections and chronic skin diseases. Restorers often handle dirty old books that contain huge amounts of mould, spores, etc. Enzymes are handled partly in solution and partly as powders. Enzymes are biologically active polypeptides whose intake may result in chronic damage. Skin contact and inhalation must be reduced.

In cleaning old books and textiles, protective measures must be taken to prevent the inhalation of dust. The dust may contain allergenic biological material such as spores, molds, polypeptides and other organic material. Occasionally the restorer has to handle dusts of heavy metals or mineral dusts such as asbestos. Toxic metals are important components of minerals and pigments. Besides the solubility of the compound, the electrochemical character is extremely important in determining the toxicity of a metal or its

compounds. Heavy metals may exist in different states of oxidation and interact with biochemical oxidation reduction processes in the body. The restorer knows this problem of oxidation reduction processes quite well from the corrosive green color on old graphics. Copper in its different states of oxidation catalyzes the formation of oxidizing species that destroy the paper.

The grape syrup of the Romans, the *sapa*, contained lead in the form of lead acetate in concentrations of 200-1000mg/l. Lead acetate has a sweet taste; an aristocrat ingested about 250 ug/day, a slave only 15 ug/day. This high daily intake of lead resulted in severe chronic damage to the members of the Roman elite because of the lead acetate intake of the aristocrats.

Dust suspensions in air are explosive as are mixtures of vapors with air. Not long ago, a dust cloud of rosin ignited in an industrial plant. The dust air mixture was ignited by a spark from a hammer during the process of grinding the lumps of rosin.

OCCUPATIONAL SAFETY AND ENVIRONMENTAL SAFETY

Fig. 2 shows how chemical compounds may act on and in the human body. Table 3 summarizes the chemical compounds mentioned in this article (I cannot guarantee the correctness of all data).

The important factors in occupational safety and environmental safety have been outlined: work with small amounts of compounds, keep the workplace clean and do not store large amounts of chemicals. Do not be frightened of chemicals, but develop a feeling for the hazards. The working style of the restorer should be pragmatic.

The simplest way of bleaching is with hypochlorite.³³ Bleaching with hydrogen peroxide strains the environment less. Here the products of the bleaching process are only water and oxygen, which are the constituents of rivers, lakes and the atmosphere. But very often this industrial bleaching process does not correspond to the goals of the restorer. In restoration processes, the uncontrolled development of oxygen from peroxide may mechanically destroy the work of art. In special cases bleaching with permanganate may be recommended. But permanganate has the disadvantage that the bleaching process cannot be controlled because of the layer of manganese dioxide formed. The wastewater contains large amounts of heavy metal. Chlorine dioxide is poisonous; it must be prepared in the workshop from chlorite and formic acid. So the use of chlorine dioxide makes a potentially hazardous supplementary reaction step necessary in the restorer's workshop.

Finally, the restorer must attempt to reduce emissions from the workplace into the environment. This goal can be reached best by the economical use of chemicals.

Chemicals react with people, pieces of art and the environment. The chemicals themselves are transformed to different chemicals during these reactions. This interaction of chemicals with living systems is demonstrated in Fig. 3; for example, methylene chloride is representative of the group of aliphatic halogenated hydrocarbons. Metabolism in the human body and in soil and water³⁴ is dominated by biochemical interactions. In the atmosphere, methylene chloride is destroyed in radical chain reactions and several intermediates are formed. All these intermediates have their own characteristic toxic profile.

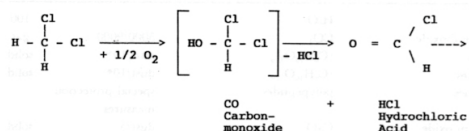
Table 3. The chemical compounds mentioned in this article

Compound	Formula	Official label	MAK (ml/m ³ or mg/m ³)	Boiling point (°C)	Molar mass (g/mol)
water	H ₂ O			100	18
carbon dioxide	CO ₂		5000/9000	gas	44
starch	(C ₆ H ₁₀ O ₅) _n		dust/10*	solid	
cellulose	(C ₆ H ₁₀ O ₅) _n		dust/10*	solid	
enzymes	polypeptides		special protection measures		
calcium oxide	CaO		dust/5	solid	56
magnesium oxide	MgO		dust/6	solid	40
calcium carbonate	CaCO ₃		dust/10*	solid	100
nitrogen dioxide	NO ₂	T	5/9	gas	46
ozone	O ₃	T	0.1/0.2	gas	48
chlorine	Cl ₂	T	0.5/1.5	gas	71
chlorine dioxide	ClO ₂	T	0.1/0.3	11	67
hypochlorite > 10% active chlorine	NaOCl/H ₂ O	C		solution	75
hydrogen peroxide in water	H ₂ O ₂ > 40% H ₂ O	C		solution	34
formaldehyde in water	CH ₂ O > 75% H ₂ O	X _n	0.5/0.6	solution	30
ethylene oxide	C ₂ H ₄ O	F*, T	carcinogen	gas	44
hydrocarbons: -CH ₂ -CH ₃					
heptane	C ₇ H ₁₆	F	500/2000	98	100
toluene	C ₇ H ₈	F, X _n	100/380	110	92
benzene	C ₆ H ₆	T	carcinogen	80	78
esters: -COOR					
methylacetate	C ₃ H ₆ O ₂	F	200/610	57	74
alcohols: -CH ₂ -OH					
ethanol	C ₂ H ₆ O	F	1000/1900	78	46
halogenated hydrocarbons: C-Cl, Br					
trichlorethylene	C ₂ HCl ₃	X _n	50/270	87	131
carbon tetrachloride	CCl ₄	T	10/65	77	154
			carcinogen		
ketones: C=O					
acetone	C ₃ H ₆ O	F	1000/2400	56	58
wood dust (oak)	C ₆ H ₁₀ O ₅		carcinogen/1*		
aflatoxin	C ₁₇ H ₁₂ O ₆		carcinogen		312
carbon black	C ₆ H ₄ O ₂		carcinogen/3.5*		
tar	C ₆ H ₄ O ₂		carcinogen		
tar oils (products from pyrolysis of organic materials)					

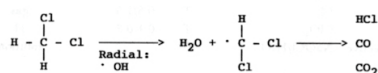
* Threshold limit value (TLV) as a time-weighted average as established by the American Conference of Governmental Industrial Hygienists.

Metabolism of CH₂Cl₂ Methylenechloride

- In the human body:



- In the Atmosphere:



- In Soil, Water:

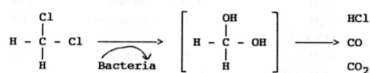


Fig. 3. Metabolism of methylene chloride

CULTURAL AND SOCIAL IMPLICATIONS

This article has emphasized safe handling in describing the interactions of chemicals in art, people and nature. But the interaction of chemicals is not just limited to the restorer's workplace but has a historical, scientific and a social component. Restorers are a minor part of the Earth's material cycles. They must stop the natural decay of objects of a high state of order, such as works of art, using labor power and skill. But, doing this work, restorers themselves must live in the present, not in the past when the work of art was

created. The compounds and the ingredients that can be used in restoration are different from those used in designing the object. Restorers have to keep learning how to handle these new substances: toxicity, long-term stability, the limits in using them and the effects on and interaction with the environment. Three examples demonstrate the change in chemical application that may be of interest to the restorer.

In coloring lignin-free papers for use as graphic papers, only anionic dyes, which are negatively charged, can be used. These dyes have the great disadvantage that they only partly adhere to the fibers. Much of the dye is discharged with the wastewater of the factories. This disadvantage was partly compensated by adding alum (aluminum potassium sulfate). Alum, which originally was used as an additive to produce water-repellent papers, catalyzes the fixation process of anionic dyes. Alum, however, also catalyzes the aging of papers, and the paper factories are therefore trying to find a replacement for alum. The dye problem was solved by newly developed cationic dyes, which carry a positive charge and adapt quite well to the fiber and reduce the wastewater pollution from paper factories.

Wood is chemically protected today, which was not true earlier. This is even true for wood used to restore old buildings. The wood is impregnated by special salt mixtures on the base of chromium, copper, boron and chromium, copper and arsenic. These salts severely strain the environment because of the high content of chromium. Newly developed organic complexes that contain copper are less hazardous to the environment and still retard mould.

Old stones used to be stabilized by soaking with water glass. Nowadays, silicon compounds are used that contain hydroxyl groups. In the stone the single molecules become polymers by condensation reactions.

The progress of science and new environmental protection laws strongly affect the work of the restorer. Restorers have to lobby to make sure that they may still use tomorrow the classical agents needed to restore pieces of art from yesterday.

Based on guidelines of the European Community, the *Gefahrstoffverordnung* (regulations on hazardous substances)¹² in Germany prohibits certain substances, mixtures and products. This means, according to § 9, paragraph 10, that water-free neutral lead carbonate, hydrocarbonate of lead and lead sulfate, which were used in colors, cannot be bought any more. These salts, of course, are important as mineral pigments for restorers. The legislation made an exception for restorers: "The use of these pigments is not prohibited in colors that are necessary for restoring pieces of art or other historic materials or for redesign of buildings under protection of law, if the use of other material is not possible." I want to emphasize the limitations placed by the last part of this sentence.

OUTLOOK: RECONNECTING STRUCTURES IN A CHEMICAL WORLD

Chemistry does not just mean isolated chemical compounds or mixtures of artificial or natural substances. Chemicals in mutual interaction may form structures that show a higher degree of evolution and intelligence than just the sum of the chemical compounds used.³⁵

Just as nature creates structures and beings from chemical compounds, the artist forms structures from substances. As nature evolves, art does, too. The goal of restorers is to save these structures, not the chemical compounds that are the base of the structures. The structures contain the information, in this case the cultural information, that must be preserved for the cultural evolution of the future. It is the special art of the work of restorers to grasp the special structural content of the piece of art and to re-prepare it correspondingly. This special art is more important for restorers' work than the use of classical chemical analysis or of physical methods of examination in restoration science.³⁶ Restoration science, on the other hand, must learn that it should broaden its repertoire of methods of analysis and examination by accepting the methods that grasp the special structures of a piece of art. One of these new methods of describing structures and whole systems is the method of image analysis and of analysis by fractal dimensions.^{37,38} Natural structures such as coastlines, leaves, particles of dust and soot have such characteristic nonintegral dimensions that are typical for their history and origin. In the same way, papers and non-woven materials can be understood in their special structures by analyzing their fractal dimensions.

SUMMARIES

The author deliberates, from the restorer's point of view, on the mutual influences and cycles of chemical compounds in nature, art and humans. Chemical compounds are the units composing structures of high order in nature and art. As Paracelsus was the first to state, the dose is crucial for the positive or negative action of a compound on its surroundings. This is true in the same way for the components of air pollution, for medicine and for the concentration and time of reaction of a chemical used to conserve an art object.

Based on this crucial fact, the author discusses the protective means and relevant rules that should be used and observed in the restoration workshop.

Produits chimiques: interactions entre art, humains et nature

L'auteur discute, du point de vue d'un restaurateur, des influences mutuelles et des cycles des composés chimiques dans la nature, l'art et les humains. Les substances chimiques sont, dans la nature et l'art, des unités composants des structures d'un ordre plus grand et, comme Paracelse l'a établi le premier, la dose est cruciale pour les composants de la pollution atmosphérique, pour les médicaments et pour la concentration et le temps de réaction d'un produit chimique utilisé pour conserver une oeuvre d'art. A partir de cette donnée essentielle, l'auteur envisage des moyens de protection et des règles pertinentes à utiliser et à observer dans l'atelier de restauration.

Chemikalien: Wechselwirkungen in Kunst, im Menschen und in der Natur

Aus dem Blickpunkt des Restaurators werden die Wechselwirkungen und Kreisläufe chemischer Stoffe in Natur, Kunst und im Menschen dargestellt. Chemische Stoffe sind die Bausteine, aus denen in der Natur und Kunst Strukturen hohen Ordnungsgrades gebildet werden. Dabei ist, wie Paracelsus erstmals formulierte, die Dosis entscheidend für die positive oder negative Wirkung, die ein Stoff oder Stoffgemisch auf die Umgebung ausübt. Dies gilt für Umweltchemikalien in der Biosphäre genauso wie für die Heil- oder Giftwirkung von Chemikalien auf den Menschen oder die Konzentration und Einwirkdauer von Chemikalien auf Kunstwerke in der Restaurierkunde. Entsprechend nehmen die Abhandlungen über Arbeitsschutz und Umweltschutz in der Werkstatt einen breiten Raum ein.

REFERENCES

1. Paracelsus, T.B. von Hohenheim (1493-1541) "Dosis sola facit venenum" 7. Defensiones, 3. Defension II 170 (1537/1538). Paracelsus: founder of medical chemistry. Endeavour 15 (1991): 147.
2. Wachter, O.: Restaurierung und Erhaltung von Büchern und Graphiken. Vienna: Bohlau, 1982.
3. Bolin, B., Degens, E. T., Kempe, S. & Ketner, P.: The global carbon cycle. New York: Wiley, 1979.
4. Wilkie, K. C. B.: Hemicellulose. Chemtech 1983: 306-319.
5. Barker, S. A.: Carbohydrates and the chemical industry: achievements and prospects. Endeavour 15 (1991): 155-157.
6. Jones, P. D.: The climate of the past 1000 years. Endeavour 14 (1990): 129-136.
7. Roberts, J. C., ed.: Paper chemistry. Glasgow: Blackie, 1991.
8. Tsuen-Hsui, T.: Science and civilisation in China. Volume 5. Chemistry and chemical technology, Part I: Paper and printing. Needham, J., ed. Cambridge: Cambridge University Press, 1985.
9. Rex, F.: Chemie und Alchemie in China. Chemie in unserer Zeit 21 (1987): 1-8.
10. Baer, N. S. & Banks, P. N.: Indoor air pollution: effects on cultural and historic materials. International Journal on Museum Management and Curatorship 4 (1985): 9-20
11. Priest, D. J.: Paper conservation: some polymeric aspects. In: Allen, N. S., Edge, M. & Horie, C. V., ed. Polymers in conservation. London: Royal Society, 1992.
12. Gefahrstoffverordnung. Verordnung über gefährliche Stoffe. Bonn: Deutscher Bundesverlag, 1991. TRGS 451/Umgang mit Gefahrstoffen im Hochschulbereich. Bundesarbeitsblatt 11 (1991): 57-74. Occupational exposure limits for airborne toxic substances: values of selected countries. Occupational Safety and Health Series No. 37. Geneva: International Labour Office, 1991.
13. Ames, B. N.: Chemicals, cancers, causalities, and cautions. Chemtech (1989): 590-598.
14. Ames, B. N. & Gold, L. S.: Falsche Annahmen über die Zusammenhänge zwischen der Umweltverschmutzung und der Entstehung von Krebs. Angewandte Chemie 102 (1990): 1233-1246. Misconceptions on pollution and the causes of cancer. Angew. Chemie Int. Ed. 29 (1990): 1197-1208.
15. Bansa, H.: Accelerated aging tests in conservation research: some ideas for a future method. Restaurator 13 (1992): 114-137.
16. Markl, H.: Die Natürlichkeit der Chemie. Die Zeit, 6.12.91.
17. Birgerson, B., Sterner, O. & Zimerson, E.: Kemiska halsorisker. Liber Hermods och forfattarna 1983. Birgerson, B., Sterner, O. & Zimerson, E.: Chemie und Gesundheit. Verlag Chemie, Weinheim 1988.
18. Richtlinien für Laboratorien. Hauptverband der gewerblichen Berufsgenossenschaften. Cologne: Carl Heymanns Verlag, 1991.

19. Merkblätter für gefährliche Arbeitsstoffe. Berufsgenossenschaft der chemischen Industrie. M-Reihe Stoff-Merkblätter insbesondere M 050. Umgang mit gesundheitsgefährlichen Stoffen. T-Reihe Technische Merkblätter. A-Reihe Allgemeine Merkblätter. Heidelberg: Jedermann Verlag, 1992.
20. Kühn, R. & Birett, K.: Merkblätter gefährliche Arbeitsstoffe. München: Ecomed.
21. Furr, A. K.: Handbook of laboratory safety. Boca Raton, FL: CRC Press, 1990.
22. Lenga, R. E.: The Sigma Aldrich Library of Chemical Safety Data. Sigma Aldrich Corp., 1992.
23. Sax, N. J.: Dangerous properties of industrial materials, Vol. I to III, New York: van Nostrand Reinhold, 1989.
24. Horrie, C. V.: Materials for conservation. Butterworths Series in Conservation and Museology. London: Butterworths, 1987.
25. Torraca, G.: Solubility and solvents for conservation problems. Rom: ICCROM, 1984.
26. Masschelein-Kleiner, L.: Les solvants. Cours de Conservation 2. Institut Royal du Patrimoine Artistique, Brussels: 1981.
27. Banik, G. & Krist, G.: Lösungsmittel in der Restaurierung. Vienna: Verlag der Apfel, 1984.
28. Doull, J., Klaassen, C. D. & Amdur, M. O.: Casarett and Doull's toxicology, the basic science of poisons, New York: Macmillan, 1980.
29. Wirth, W. & Gloxhuber, C.: Toxikologie. Stuttgart: Thieme, 1981.
30. Sicherheit im Labor. Sicherheitsdatenblätter für Lösungsmittel. Darmstadt: Merck, 1992.
31. Koch, R.: Umweltchemikalien. Weinheim: VCH-Publishers, 1989.
32. Hua, H.: Fischer, W. & Fath, M.: Machinery for paper restoration. Restaurator 10 (1989). 83-99.
33. Ströfer-Hua, E.: Classical methods of bleaching in the restoration workshop: the role of the OH radical. Restaurator 12 (1991): 131-135.
34. Müller, R. & Lingers, F.: Mikrobieller Abbau halogener Kohlenwasserstoffe: Ein Beitrag zur Lösung vieler Umweltprobleme? Angewandte Chemie 98 (1986): 778-787. Microbial degradation of halogenated hydrocarbons: a biological solution to pollution problems? Angew. Chemie Int. Ed. 25 (1986): 779*789.
35. Prigogine, I.: From being to becoming- time and complexity in physical sciences. Vom Sein zum Werden - Zeit und Komplexität in den Naturwissenschaften. München: Piper, 1979.
36. Beilby, A. L.: Art, archaeology, and analytical chemistry. J. Chem. Education 69 (1992): 437-438 and cited literature.
37. Doyle, R. D. & Doyle, E. B.: The application of computer image processing to artifact analysis as applied to the Shroud of Turin study. Studies in Conservation 31 (1986): 1-6.
38. Kaye, B. H.: Discovering the surprising patterns of chaos and complexity. Weinheim: VCH Publishers, 1992.
39. Calvini, P.: Computer simulation of heterogeneous degradation of paper: theory and some experimental results, Paper Conservator (in press).