

PLASTICS AND THEIR OCCUPATIONAL HEALTH IMPORTANCE

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One cannot imagine any more daily life without plastics. While previously men had to be satisfied with substances of natural origin, in the last decades the chemical industry created an abundance of plastics on synthetic base, which are far superior to the natural substances with regard to their applicability. If one follows the economic journals and the professional publications of the pertinent industries and if one takes into consideration the industrial expositions, one can see, that also we here Germany have found since 1945, with tenacious work, connection to the manufacturing of the new plastics. Thereby it is interesting to know, that West Germany became since 1953 the second greatest plastic producer, after the USA, of plastic products.

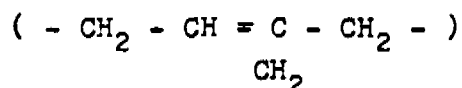
The field of plastics has been widened especially in the last years such an extent, that it would go too far to deal within the framework of a short treatise with these substances and their occupational medical importances. Therefore, a limitation to certain chemically used groups is indispensably necessary. Also the chemical bases of the plastics can only be touched here, the intermediary products at the preparation can be mentioned only if they are important and the chemical formulae can be pointed out in simplified form only then when it is absolutely important for the comprehension.

It proves to be necessary to maintain a certain scheme, when discussing plastic materials, which returns always in the pertinent chemical and technical professional books. The producing companies designate the plastics with trade marks, which shall be also here, mentioned shortly.

For the following statements, let us point out again, that the plastics of today, as already mentioned, can be considered in no case more than substitute materials. The plastics, produced in planned research products, which have, mainly, properties, which cannot be found in natural products, especially not without technical finishing.

Let us deal first with the modified natural substances, whereby natural rubber, cellulose, animal and vegetable proteins, as well as resins, colophonium and dry oil are improved with chemical conversions into so called plastics.

From natural rubber, which has as base the isoprene molecule



one can prepare plastics by isomerization, oxidation, chlorination and adding acids, as well as by introducing fillers. The chemical conversions indicate already here the acting possibilities of acid and acid vapors, as well as of chlorine. These actions on the human body are so generally known, that we must not go into this in more details here. The ready made plastic products of this kind do not have any health hazards in their further finishing. From the abundance of trade marks, let us single out here :

- cyclo rubber by isomerization - thermoprene, oxidized rubber - Rubbon
chlorinated rubber - Pergut, Alloprene and rubber hydrochloride - Pliofil

Cellulose - $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ - is converted into plastics by dissolution, esterification and etherification, as well as by introducing metal salts. Known are: regenerated cellulose as artificial silk, cellulose acetate and cellulosenitrate as Cellon or Celluloid, the ethers of cellulose as methy

celluloses for lacquer raw materials and vulcanized fiber, prepared by adding fillers. The danger in these fabrications is the corrosion possibility by the lyes, influences by carbon disulfide, hydrogen sulfide, acetic acid, acetic acid anhydride and similars. The methods of preparation are already since years known, so that the influence of chemical substances can be extensively eliminated by appropriate measures at the manufacturing, such as casing of the apparatus, sucking off, etc. In the manufacturing of artificial silk sometimes also the known eye phenomena appear.

The easily combustible celluloid is replaced today manifold by Cello which is prepared from acetate cellulose, by adding the gelatinizing agent tricresylphosphate $(CH_3C_6H_4)_3PO_4$. Later we shall deal again with the last mentioned chemical compound, because from the point of view of occupational health, its orthocompounds are of importance.

Very well known are the plastics, prepared by Formalin hardening of animal and vegetable albumins, such as casein plastics, Galalith, or Lanital. The skin irritations of the uncovered parts of the body, the irritations of the ocular conjunctive and the influence on the upper respiratory tracks by formaldehyde are known.

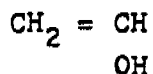
Finally, colophonium resins and dry oils are converted into plastics by salt formation, esterification, oxidation and building in phenols. They find many applications under the names of "Albertol" and "Beckacite", as lacquering raw materials. From industrial ^{hygiene} point of view they are not of special importance.

Let us discuss now the true plastic materials, which are prepared synthetically by polymerization, or condensation. Starting materials for the plastics are: chalk, coal, oxygen and nitrogen, furthermore in cracking

processes treated petroleum, alcohol and watergas. There is here an abundance of plastics, and it is amazing in what extent the organic synthesis developed in this field. The intermediary products, at the preparation of plastics are so numerous, that it would need a separate discussion to enumerate all from industrial hygiene point of view. In first place, let us elucidate the end products, which find as plastics comprehensive use in all branches of technology and economy. Starting from chalk and coal, over carbide and acetylene at the synthesis through different chemical conversions, one obtains the polyvinyl products, such as polyvinylalcohol-, ether-, chloride-, carbazole-, acetate, polymethylacrylic acid methylesters, polychloroprene and polybutadiene.

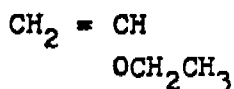
With regard to indications to possible action, let us enumerate at random some of them.

Polyvinyl alcohol from vinyl alcohol



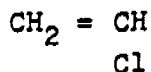
known under the trade mark Polyviol, is used as thermoplast. From this material e.g. aprons, gloves and similar are prepared. During the manufacturing several times irritation of the skin occurred.

Polyvinyl ether from vinyl ether



under the trade mark Igevin, is used as thermoplast and adhesive, no health hazard properties are known.

Polyvinylchloride and mix-polymerizate from vinylchloride

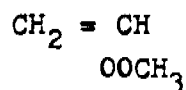


known under the trade marks Igelit - Mipolam, has multiple use to prepare

commodities, aprons, raincoats. Depending on the addition of plasticizers also soft-Igelite can be prepared. Let us point out here the earlier mentioned harmful action of soft gelites, where tricresylphosphate is used as plasticizer, which is very poisonous in its ortho compound. The action of tricresylphosphate shall be discussed in more details with the plasticizers. The mentioned harms do not occur any more when phthalate plasticizers are used.

Polyvinylcarbazole from vinyl carbazole, known under the trade mark Luvikan, is used manifold as thermoplastic; it is remarkable, that exzema phenomena can be triggered.

Polyvinylacetate from vinylacetate



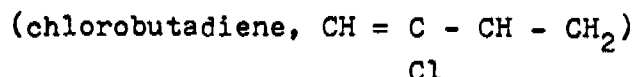
trade mark, Mowilith, or Vinnapas, is also a thermoplast, can cause skin irritation, when irritating plasticizers, or hardeners are used and the compound is not reacted chemically completely.

Polymethylacrylicacidmethyl ester from acetone over methylacrylicacid ester finds manifold use under the trade mark Plexiglas. In this respect the acrylonitrile, as intermediary product is very important from occupational hygiene point of view. The preparation of acrylonitrile widens always more and more because it can be used also for the preparation of other plastics, such as e.g. the synthetic Buna rubbers. Acrylonitrile ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$) can be perceived only at dangerous concentration with odor sense. The poisonous effect is probably a direct action of the acrylonitrile molecule, possible also by cleaving cyanogen in the organism. The symptoms of poisoning are similar to the cyanide poisoning. By inhaling small, with odor sense no more perceivable amounts, do most poisoning occur. When acrylonitrile is used, under the name Ventox, as insecticide, a strong smelling warning substance must be added to it.

In animal research by acrylonitrile, irritation of the mucous membrane, anoxemia, increased secretion of thiocyanate in the urine and death by respiratory paralysis, were observed.

Polychloroprene is a synthetic rubber, known under the trade marks Neoprene, Buna, etc. For clarity's sake, let us mention, that from chlorobutadiene polychloroprene and from butadiene polybutadiene is prepared; from the latter by converting with styrene (vinylbenzene) Buna S and with acrylonitrile Perbunan were prepared.

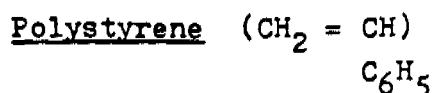
Chloroprene



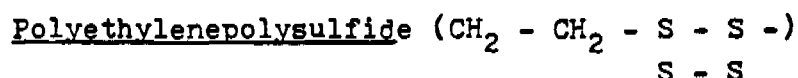
caused poisoning. When inhaled in larger amounts, narcotic phenomena occur with respiratory paralysis. Those workers, employed at the chloroprene distillation are often remarkably tired, have a distinct pressure sensation in the chest, before all below the sternum in the area of the trachea connected with dyspnea and palpitation of the heart; typical is also a remarkable irritability. Among the workers in the polymerization unit, loss of hair on the head can occur, already one month after the starting of the contact with chloroprene. When taken out from this unit, the hair on the head starts growing again.

Now, let us mention shortly a group of plastics, which are prepared from coal, by coking.

To these belong the aniline resin from aniline ($\text{C}_6\text{H}_5\text{NH}_2$), named Iga: which is used for compressed masses and hard paper. When one operates with aniline, the general safety measures must be observed; the influences of aniline on the human body are presumably known.



named also Trolitul, is not specially toxic, as this could be ascertained in animal research. At the preparation of styrene (vinylbenzene) special care must be taken, since the aluminumchloride, resp. - hydroxyde, used as catalyst can have a very corrosive influence.



with the trade mark Thiokol, Perduren, is an oil resistant synthetic rubber which is used to impregnate synthetic leather. At the influence of skin perspiration, skin irritations can occur.

Phenol-, and cresol resins, named Bakelite, Albertite, Resinole, are used as settable synthetic resins and compressed masses. Skin irritations by synthetic resin solutions on basis of formaldehyde, phenol-, and cresol condensation products were reported, important is here the over sensitivity towards formaldehyde. The dermatitis takes place with strong itch: lasts often for a long time and has the tendency to recidivation. Also irritations of the mucous membrane of the nose, the upper and deeper respiratory tracks occur. Most irritations can be avoided, when at the introduction of the often fine article, no dust formation takes place. But some kind of sucking measures are not appropriate on account of the light weight of the dry goods. Therefore one must see to it, that before all at the manufacturing of plastics of the phenol form -aldehyde series the apparatus should be jacketed and at times, the workers should wear face shields. Before all care must be taken, that well hardened, i.e. chemically well bound plastic masses are finished, which do not evolve excess formaldehyde.

Phthalate resins, or maleic resins are used as lacquering raw materi
Intermediary products are phthalicacid-anhydride over ethanol, pentaeryth
rite. Here practically no toxic effects are known, merely irritations of
the mucous membranes, when working for a longer time with these substances

Furthermore, let us mention urea and thiourea resins (carbamide resi
These substances are, beside their known fields of application, accelerat
ors at the vulcanization. They irritate the respiratory tracks and the
skin.

The chlorinated naphthalene and diphenyls gained importance in recen
years under the name Perna, as synthetic resin in the electro-industr
The more chlorine atoms are introduced in these compounds, the more toxi
they become. The most dangerous are the penta-, and hexachloro-compounds
The vapors, liberated at the heating of e.g. soldering of therewith insul
ated electric wires, are extremely toxic. The endangered units must have
very good ventilation. The toxic effect attacks, according to American
sources, before all the liver cells, serious jaundice and acute yellow li
atrophy are described.

Plastic fabrics from polyamide have found application especially in
the textile industry, and here again, before all in the clothing and ho-
sieri industry. To the polyamides belong the, for the first time in Ger-
many manufactured Perlon and the, in the USA developed Nylon. While Perlc
is used mainly in hosiery, Nylon is used more in the clothing industry as
substitute for silk. From the two polyamides, Perlon and Nylon, today, fir
fabrics are prepared with better qualities, than previously. The textiles,
made from these chemical substances loose only seldom their shape, do not
crease, are easily washable and dry fast.

From occupational hygienic point of view, one must mention here, that at the finishing of extremely stable and solid fibers in the hosiery industry, mechanical damages of the finger-tips and the surface of the palms can take place at stenter workers and warp-knitters, whereby, seldom also secondary infections can occur. So, in case of a female warp knit worker an occupational disease, liable to indemnity, had to be recognized because according to the course and repeated recidivation as well as the result of the skin tests, Perlon was detected as occupational toxic substance. In this connection, let us mention also, that this warp-knit worker was over-sensitive to pure silk. Since skin tests with synthetic silk did not show any over sensitivity, this highly qualified worker could continue to work in her profession at the finishing of synthetic silk (viscose synthetic silk - acetate synthetic silk). In the field of the state industrial physician in Bavaria, a case of oversensitivity towards Nylon could be ascertained. Redness of the skin as far as covered with the hosiery was observed. But the skin phenomena caused by Perlon and Nylon disappeared, when the harmful noxious substance was removed. The skin irritations, designated as Nylon dermatitis, were observed after wearing Nylon stockings, first in the USA. Thereby it turned out, that undyed Nylon fiber is only seldom the cause of dermatitis. Therefore also the dye of the Nylon tissue was tested, whether it might be cause of the dermatitis. Thereby, actually some dyes were found as toxic, e.g. black Nylon stockings, which were, evidently, not rinsed sufficiently after dyeing, caused dermatitis. After the examinations, one can state, that the polyamides, Nylon and Perlon, must be considered as good skinfriendly, on the other hand, no doubt, chemicals, which serve as finishings for these plastics, or are brought otherwise in contact with them, can trigger skin reactions.

So, e.g. one should avoid to wear Perlon hair nets, when resorcinol containing hair lotions are used. Also not sufficiently chemically reacted Nylon-, or Perlon-products can cause dermatitis. Nylon-, and Perlon filaments are used also in e.g. surgery; Perlon nets heal well in case of abdominal ruptures. Examinations hitherto have shown, that men and animal respond in the same way to bodyforeign substances, and an even, cell-poor connecting tissue surrounds the polyamide implantation and according to the results of the experiments, there is no increased cancer danger when polyamide, especially the type Supramide is used. But recent experiments have demonstrated, that polyamide dusts (caprolactam) when introduced into the cavity of the abdomen bring about there a foreign body-granulate tissue, which transforms after months into a caseous necrosis, supplied with calcium sediments, is surrounded with a lumpy capsule and reminds to the happening at tuberculosis. The purpose of further examinations will be to ascertain, how the lung tissues react to the effect of polyamide dusts. But these most recent examinations show, when handling plastics of the polyamide series, and especially in form of dust, care must be taken.

A group of plastics, which found especially wide acceptance in recent times is the polyurethane. The basic substances of this plastic are the resp. polyisocyanates, which yield in the presence of catalysts polyurethanes. The di-, or polyisocyanates are designated as Desmodur and the polyesters as Desmophen. While the end products, that is the polyurethane and the Desmophen-types are harmless, the Desmodurs, insofar as they are volatile, are toxic in the sense as irritating substances to the respiratory and stomach mucous membranes. After an interval period, very severe bronchitis and bronchopneumonia, as well as subsequently very asthmatic states are observed. Since the isocyanates are used increasingly also for the p

paration of polyurethane lacquers, at the spray-painting and brush painting with such lacquers great care must be taken. Similar phenomena can develop at the preparation of foams, Moltopren, whereby when Desmodur and Demophene are joined by reaction heat, an evaporation of Desmodure can take place. From the series of these plastics let us mention also Vulkollan, a substance similar to hard rubber as well as the adhesive, Polystal.

Silicones are a completely new group of plastic, which were developed first in the USA. Also in Germany the preparation of silicones was accepted and they gained in the practice always more importance on account of their multiple useability in the industry, pharmacy, and medicine. The silicones, scientifically the organopolysiloxanes are highmolecular synthetic substances, which are built up from silicon and oxygen, and the free valencies of which are saturated by organic radicals, such as methyl-, and methylphenyl groups, as well as chlorine. From the original oily silicon by adding fillers, fatty, resinous and rubberlike products form and also plastic masses, which distinguish themselves by biological compatibility.

It would be too much to report here about the chemical syntheses of these plastics in more details, but let us point out, that by methylation with chloromethyl such liquids, silanes, result, which separate chlorine and act irritatingly on the mucous membranes of the upper and deeper respiratory air passages. The influence of methylenechloride, which is also used in the cryogenic industry in many ways, is noticeable in local irritations and narcotic phenomena. We can see, thus, that in the course of manufacturing health damaging influences can occur. To meet these, the apparatus must be kept tight; against suddenly occurring leakiness of the apparatus gas masks must be in preparedness.

The silicones themselves are a class of plastics without special toxicity. With this substance in the USA and also in Germany experiments were carried on on rats, rabbits and guinea pigs. In incorporating silicon by feeding, or injecting subcutaneously and in the peritoneum, as well as by dropwise introducing in the ocular conjunctive sack, no specific foreign body reactions and no toxic side reactions were observed. As already mentioned a certain danger exists only at the manufacturing.

It is not essential to treat comprehensively the different application possibilities of silicone in such a short report. The silicones are indifferent within a certain temperature range (lubricant), they can be used as base for ointments, without causing dermatitis, they are used as anti-foaming agents and can be applied as resin in fireproof forms. So, e.g. silicon resin is calcinated in baking bread moulds; these mouldings can be then used very often. The silicones serve also as lacquer substances and as sealing material.

In connection to the silicones, let us mention another plastic material which contains in a chain arranged carbon and fluorine: it has been developed in the USA under the designation Teflon, and has the trade mark Fluon. The properties of this plastic are very remarkable. It distinguishes itself, similar to the silicones, by high thermal stability and on account of its stability at low temperatures. Furthermore, it is very chemically resistant especially to hydrofluoric acid, nitric acid and hydrochloric acid; the electric properties are described as outstanding. The plastic, Teflon is chemically a polytetrafluoroethylene.

In the course of further finishing e.g. when heated above 110°C , harmful gaseous products can form. Analogously to metal vapor-, or foundry-fever, here a polymer vapor fever is described. After a symptomfree inter-

val, symptoms of chest anxiety and throat irritation occur, and the temperature can rise suddenly. Observations show, that the occupation with this plastic at high temperatures causes severe irritation of the respiratory passages, and can occur even in form of lung edema.

Finally let us mention shortly the so-called plasticizers, or gelating agents. The plasticizers unite with organic film formers, dissolve and not dissolved, into homogeneous products; they influence the filmforming agents in a certain way with respect to the hardness, the flexibility and the gloss of the film (organic filmforming agents, nitrate cellulose acetyl celluloses, rubber, resin and similars.). In a larger sense, one understands under plasticizers also substances, which make a fabric of go feel and supple. Such kinds are used, e.g. in the leather-, and synthetic leather industry. The plasticizers and solvents are marketed under trade names. Let us choose some at random.

Tricresylphosphate. In the tricresylphosphate the ortho-bonding is toxic. Tricresylphosphate caused during the war and in the post war sometimes serious poisonings, especially when confused with edible oil. The poisonings cause first acute stomach-intestine-irritations, then preponderantly motoric paralyses in form of polyneuritis and also damages in the spinal cord.

As already indicated, the plasticizer tricresylphosphate was used for the modification of Igelit, and e.g. by wearing aprons from Igelit, or sandals from Igelit the above mentioned disease symptoms can appear in more or less gross form. This was explained so, that the absorption of the ortho-tricresylphosphate, contained in the Igelit, through the moist skin, occurred under the influence of steam and heat. Today such poisonings, which happened also when Igelit hoses were used for the spirits distillate and at the transportation of butter in Igelit-foils, belongs to the past, because today for such purposes levelling plasticizers on phthalic acid base are used.

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Diethylphthalate, named also Palatinol has low toxicity and does not trigger any erythema and other skin reactions, but it can act slightly irritating to the mucous membranes.

Among the chlorinated hydrocarbons worth mentioning is the symmetric dichloroethane - $\text{CH}_2\text{Cl} - \text{CH}_2\text{Cl}$ -, of which, from the textbooks and reference works, one has the impression, that it is from industrial hygiene point of view not especially remarkable. Recently, however, it was noticed that special care must be taken at the place, where it is used. We must count here, before all, with a hepatorenal symptom complex in case of severe acute intoxications, while the intoxicating danger in chronic poisoning by acute subtoxic concentrations is relatively small. The toxicology of dichloroethane corresponds farreachingly to that of carbon tetrachloride. The unobjectionable limit concentration is for dichloroethane, however, lower than for carbon tetrachloride, according to American sources.

Benzylacetate, named Plastolin, has a narcotic effect. But this regresses, in general, as at the esters, behind irritating effects. Industrial poisonings are hitherto almost unknown.

Cyclohexanol, named Anol, or Hexaline, is known in industrial useage by its light pre-narcotic and cathartic symptoms, but it has not the specific action of benzene.

Decahydronaphthalene, named Dekalin, has a slight irritating effect, which is expressed in catarrh, coughing and reddening of the eyes; also exzema were observed. The narcotic effect is very small. Other specific effects are not known.

With this short report, we wanted to give a survey about the industrial hazards of plastics. The survey shows, that the plastics, in their pr

perties as end products are, in general, extremely indifferent from health hazards point of view. The health hazards lie, first of all, in the intermediary products and in some admixtures. The recent research on the influence of polyamide dusts, show, however, that under certain circumstances, disease phenomena can appear. Therefore the further task of the industrial hygienic and toxicologic research is to explain in more details the question of the influence of plastics on the human body.