J. industr. Med., 1953, **10**, 255.

HEALTH PROBLEMS IN THE MANUFACTURE AND USE OF PLASTICS

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(RECEIVED FOR PUBLICATION JUNE 8, 1953)

The increasing variety of plastic materials produced during the last few years is due mainly to the ability of the modern chemist to synthesize the chemical compounds from which plastics are made. The basis of most plastics today is the synthetic resin and its introduction has made available new substances hitherto unknown in industry. Modern plastics are manufactured to serve specific purposes so that the synthetic polymers can no longer be regarded as substitutes for those found naturally as cellulose, rubber, and proteins. A wide range of materials can be made from them and so designed as to meet the actual properties required for any particular application.

In addition to the polymer, synthetic plastic materials contain varying amounts of other chemicals as catalysts, accelerators, stabilizers, hardeners, fillers, and so on, which are added to assist or regulate polymerization or to influence the properties of the final material, such as colour and flexibility. Most polymers are chemically inert and in ordinary circumstances the final plastic material should be comparatively harmless. It is practically difficult, however, in practice to effect complete polymerization and traces of free monomer or other chemicals may be present which can sometimes produce pathological conditions such as dermatitis.

Polymerized chemicals may be broadly divided into two groups, condensation and addition polymers. They may also be divided into thermoplastic and thermosetting types depending upon whether the material is softened or hardened by heating. The change that takes place on heating the thermosetting material is irreversible.

CONDENSATION POLYMER PLASTICS

Condensation polymers are usually formed by the union of molecules with the elimination of water or other compounds.

Formaldehyde Products

The thermosetting types in this group are those formed by the condensation of phenol, cresol, urea, or melamine with formaldehyde. In the manufacture and use of resins, glues, and moulding powders of this type free formaldehyde may be liberated under certain circumstances, the amount depending on such factors as the ratio of the ingredients, the degree of condensation, and the addition of other chemicals such as hexamethylenetetramine. For the sake of simplicity these products are discussed below in two separate sections depending upon whether they mainly affect the human body externally or internally.

Effects on the Skin.—Formaldehyde and hexamine are well known as primary irritants of the skin and mucous membranes and many factories handling resin glues have had cases of dermatitis at some time or another (Factory Department, 1943). Schwartz, Peck, and Dunn (1943) mention a factory of 800 employees where 600 cases of glue dermatitis occurred during the first six months of operation. In a small leather factory the incidence of dermatitis was highest (28%) in the section where "notorious sensitisers such as formaldehyde, lacquer and Bismarck Brown were used" (Squire, Cruickshank, and Topley, 1950). It has been stated that the actual substance responsible for hexamine and formaldehyde dermatitis is formic acid (Schwartz, Tulipan, and Peck, 1947).

There is another factor that should be considered in assessing the predominant cause of dermatitis as the result of handling some of these products. In their usual commercial form, for example, these formaldehyde glues and resins will adhere to the skin and rapidly harden on contact with it, and Little (1950) considers this to be the primary cause of the more serious outbreaks of dermatitis from them.

Mayers and Silverburg (1936) stress the great variation in the length of time ranging from a few

...gers and dorsa which reacted very slowly to ... although the oedema of the face subsided ... day or two. Shortly afterwards he took a ...ght's holiday when the condition cleared entirely.

The third type of lesion is one in which the ...ption may combine the clinical features of the ...two types described above.

Case 4.—A maintenance fitter, aged 62, developed dermatitis after working on machines contaminated by ... formaldehyde dust. This affected only the hands and arms in the first place and he was removed from the job and given work as a storekeeper following which the condition healed. While in the stores he was one day inadvertently handed a number of valves contaminated with urea formaldehyde powder and within a few hours ... had developed a sensitization eczema affecting the ... hands, forearms, axillae, scrotum, and groins. He was taken off work altogether and only slowly responded to treatment extending over a period of weeks. On his return to work he complained that he felt an immediate tingling of his eyes and face even when he entered the factory for a few moments as he did contrary to instructions on one or two occasions. He was finally given work as a commissionaire in a laboratory building far removed from the factory itself and he has had no further trouble during the last few years.

The problem of permanent alternative work for dermatitis cases presents difficulties, and Squire and others (1950) have rightly stressed that each individual case must be given serious consideration before a decision is made one way or the other. It has been found that most cases of dermatitis from formaldehyde occurring in this group of factories become sensitized to it so that they seem more liable to a skin eruption subsequently but a few develop an immunity or possibly take greater care on returning to their work. This is in agreement with Schwartz (1945) but contrary to his opinion urea formaldehyde resins seem to be as potent a cause of ... as phenol formaldehyde preparations. ...may be due to the fact that in the cases described by him the glues and resins were of that composition which rapidly hardened on contact with the skin.

... small factory manufacturing urea and ... formaldehyde resins, glues, and moulding ... the number of cases of dermatitis were ... relatively few as can be seen in the accompanying table. This factory employed an average of ... 150 and 250 men at any one time over a ... of years but since the labour turnover was ... many more individuals than the average number ... exposed to risk during each year.

The table shows that the amount of time lost ... tends to diminish in spite of the marked ... production. An interesting feature is the large percentage of time lost by a small number of men. Eighty per cent. of the total time lost was caused by five men (more than half of this was due to one man). Seventy-seven per cent. of the total number of cases of dermatitis lost no time and were successfully treated while continuing to work—occasionally at the same job. During the last two years (1949–1950) only four men lost time and between them accounted for less than 5% of the total time lost through dermatitis.

Year	Production (1945 = 100)	Dermatitis Cases	Hours Lost	Lost Time Cases
1945	100	9	1,238	1
1946	150	10	1,592	6
1947	194	11	80	1
1948	260	9	208	4
1949	370	16	96	2
1950	447	15	39	2

Effects on Absorption.—The acute effects of formaldehyde vapour on the eyes and respiratory passages are well known; they are frequently produced by vapour concentrations as low as 20 to 30 p.p.m. Lower concentrations may result in watering of the eyes, irritation of the throat and upper respiratory tract (Barnes and Speicher, 1942), but these symptoms often disappear after a short interval (10–30 minutes) as the worker gradually becomes accustomed to the vapour. The inhalation of high concentrations has been shown to produce pulmonary oedema and haemorrhage but the pungency of the vapour usually makes it impossible to remain in atmospheres contaminated to such an extent. The extensive literature on its toxicity is well summarized by the U.S. Public Health Service (1945), but in spite of the vast number of investigations which have been undertaken there is a notable lack of information and conformity of opinion on the possible chronic effects in man produced by the repeated absorption of small quantities over a long period of time.

Fischer (1905) asserts that the inhalation of the gas even in small quantities is followed by bronchitis and pneumonia but few other investigators agree with this statement. A case is quoted by Lile (1910) of a tuberculous patient who was kept in a room saturated with formaldehyde gas for several weeks, during which time the patient actually gained weight and his physical condition apparently improved. These effects are surprising even though the actual atmospheric concentration of formaldehyde in the room is not known. The term "saturated" conveys very little except that the concentration was presumably high. It is possible for men to work without embarrassment in atmospheres contaminated with formaldehyde to an

TABLE I

CLINICAL DATA OF 25 MEN EXPOSED TO FORMALDEHYDE VAPOUR

No.	Age	No. of Years Employed	Weight st.	Weight lb.	Blood Pressure	Summary of x-Ray Report of Chest	Complete Blood Count	Other Findings
1	49	13	10	5	140 80	Normal	Normal	Dermatitis (lasted [illegible] days—no time lost)
2	46	10	8	3	110 65	Normal	White cells 10,500	—
3	49	5½	10	2	120 65	Old healed focus right upper zone	White cells 11,400	—
4	50	6½	11	5	110 70	Normal	Normal	—
5	47	7½	10	2	120 70	Suggestion of basal bronchiectasis. Old healed focus right upper zone. No evidence of activity	White cells 13,900	Clinical chronic emphysema. Changed his job, left the factory shortly after examination
6	51	6½	9	10	126 80	Normal	White cells 4,100	—
7	43	7½	9	11	110 70	Normal	Normal	—
8	51	11	10	10½	120 80	Normal	Normal	—
9	45	18	7	13	145 90	Normal	Hb. 92%	—
10	48	10½	11	5½	130 80	Normal	White cells 13,250	—
11	38	5	11	3½	140 70	Normal	White cells 12,800	—
12	40	8	10	5	145 90	Normal	Normal	—
13	24	9½	12	5½	120 70	Normal	Normal	—
14	57	6	7	12½	120 65	Old healed focus left upper zone. No evidence of activity	White cells 11,700	Dermatitis—no time lost. Chest radiograph two years later showed no change from his previous report
15	35	9	7	11	120 70	Calcified hilar glands	Normal	—
16	61	7	10	1½	160 115	Cardiac enlargement—ventricular hypertrophy. No pulmonary disease	Normal	Cardiac enlargement—confirmed clinically. (Triple rhythm) aortic 2nd+. Pulmonary bases clear. Some evidence of hypertensive retinitis. Urine, albumin+ +
17	54	6	8	8	140 80	Increased vascular shadows	White cells 14,900	"Arthritis", left elbow and right knee
18	37	5½	10	2½	130 80	Normal	Normal	—
19	38	11	8	0½	120 70	Normal	White cells 4,500	—
20	43	6	10	11½	150 85	Cardiac enlargement consistent with hypertension. Increased vascular shadows. No pulmonary disease	White cells 11,800	—
21	46	5½	13	10½	170 100	Cardiac enlargement. Vascular shadows increased. No pulmonary disease	White cells 14,100	—
22	46	13	9	6	180 75	Old focus right apex. Shadow left apex. No evidence of activity	R.B.C. 4,860,000 Hb 88%. White cells 10,000	Dermatitis mildly on two occasions. No time lost. Chest radiograph one year later—no change from previous report
23	49	5	9	8	120 80	Emphysema. Fibrosis both apices and upper zones, probably old infiltration. No evidence of activity	Normal	Mild dermatitis (no time lost). Keratosis palmaris.
24	44	6	10	2½	120 80	Normal	Normal	—
25	37	8	9	10½	120 65	Slight increased shadows lower zones	Normal	—

... al. Mallette and von Haam (1952) ... that dioctyl phthalate administered intra... really in comparatively large doses proved ... animals, but no delayed effect or permanent ... was noted in surviving animals.

Tetrafluorethylene ($CF_2=CF_2$)

The substitution of four fluorine for the hydrogen ... ms of ethylene produces an unstable reactive gas ... n as tetrafluorethylene. This and its poly... ized form have been discussed in a previous ... which describes the toxic effects of the ... mer under certain exceptional conditions ... ms, 1951).

Methyl Methacrylate ($CH_2: C [CH_3] COOCH_3$)

Methyl methacrylate, B.P. 100°C, is a colourless ... d with a sweetish, characteristic odour.

It is a mild irritant of the mucous membranes and ... few instances has been known to produce ... matitis. Spealman, Main, Haag, and Larson ... 45) state that the instillation of three drops of ... monomer into the eye of a rabbit produced ... mediate irritation with inflammation and ... dema within a few hours. Complete recovery ... curred after three days. On the skin it produced ... very mild irritation which was fleeting in its ... fects. The writers also describe the toxicity ... the monomer when administered to various ... mals subcutaneously, intraperitoneally, orally ... by inhalation, and pathological changes ... found in the livers and kidneys resembling ... lesions produced by carbon tetrachloride. ... is interesting to note that changes were ... nd in the lungs due to its irritant action ... en in some instances were apparently reversible ... ce healing subsequently occurred.

The same investigators submitted 50 volunteers ... tch tests with the result that about one-third ... the total developed a mild erythema in 48 hours. ... at 20% showed evidence of having developed ... nsitivity to the monomer when tested ten days ... Polymerized methyl methacrylate similarly ... produced no effects.

The toxicity of the monomer when absorbed by ... perimental animals has been described by ... man (1941) who also mentioned its irritant ... ct on the mucous membranes when inhaled. His ... periments show that when absorbed in toxic ... antities methyl methacrylate causes an increasing ... weakness, decreased respiration, dyspnoea, ... loss of reflex activity; the animals finally died ... ath as the result of respiratory failure.

... atmospheric concentration of methyl metha... should be maintained below 1,000 parts per million if working conditions are to be regarded as satisfactory. Its odour can be detected at far lower concentrations.

Cases of dermatitis due to handling this monomer are not common and the few that have occurred in the present group of factories have been of a mild nature, quickly responding to alternative work.

Case 6.—This man, aged 42, was engaged in making decorative plastic models. A great deal of the work was done with bare hands which involved fairly gross contamination with the liquid monomer and compositions containing it. He developed interdigital eczema of both hands but failed to report the condition to the ambulance room for a matter of four or five weeks. When first seen he had a dry, scaling eczema between the fingers of both hands and a papular erythema of the right forearm. This gradually cleared with local treatment and alternative work.

A few cases of dermatitis have been reported in dental mechanics using polymethacrylate and its monomer in the manufacture of dental prostheses. In such instances working conditions are often unsatisfactory so that it is very important to establish the real cause of the skin eruption and patch tests may be of value in these cases. Dental mechanics may be exposed to other irritants than methyl methacrylate and in some instances the use of abrasives (e.g. pumice powder) may have been the cause of the skin eruption.

Polymethyl Methacrylate

Under certain circumstances methyl methacrylate can be converted into a solid polymer that constitutes the basis of many commercial preparations known under the trade names "perspex", "lucite", "plexiglas", "diakon", "kallodent", etc. These commercial preparations vary in composition and may contain other chemicals besides the polymer. A brief history of the monomer together with a detailed description of the chemistry, the properties and some of the applications of the polymer have been given by Caress (1944).

The final polymer is like many others comparatively inert, e.g. it is used in the manufacture of contact lenses, artificial teeth, splints, and surgical instruments. Wilson (1946) has quoted 25 patients who had extrapleural pneumolyses by means of methyl methacrylate plombage. According to him the material fulfills all the essential criteria of an ideal for plombage, and "it is non-irritating to the human body". For this operation the "methyl methacrylate was moulded into solid and hollow balls" so that it is obvious the writer means the polymerized form although he uses the term methyl methacrylate (the monomer) throughout his paper.

... may become dangerous under comparatively normal circumstances. It also stresses the importance of taking a full history and paying particular attention in this instance to the chemistry of the materials involved.

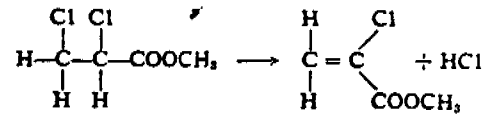
Case 10.—This laboratory worker, aged 24, was handling methyl α β dichlorpropionate and spilled some of the liquid on to his left hand. He washed it off in the usual way and thought no more of it since previous experience had shown the chemical to be quite harmless. About three to four hours later he felt some irritation beneath the watch strap on his left wrist and thinking it was chafing his skin he transferred the watch to the other wrist. Two hours later he noticed irritation of the right wrist. The following morning when he reported to the ambulance room there were erythematous areas on both wrists. These were covered with tulle gras dressings.

The following day he was away from the district in spite of the fact that the areas had now blistered and he did not report to the ambulance room again until the next day. By this time he had large blisters on the anterior surfaces of both wrists (Fig. 2). The one on the left wrist measured 3 in. × 2 in. × ¾ in. They were incised, the fluid gently evacuated and the blistered skin allowed to collapse. Subsequent dressings with tulle gras produced rapid healing.

Fig. 1.—Vesicular eruption from exposure to methyl α chloracrylate.

Fig. 2.—Large blisters on both wrists following exposure to methyl α β dichlorpropionate.

Methyl α β dichlorpropionate readily loses a molecule of HCl to become the powerful vesicant methyl α chloracrylate.



This must have occurred on the skin beneath the wrist-watch strap through which the original substance had penetrated.

Effect of the Vapour on the Eyes.—The vapour of methyl chloracrylate is markedly irritant even in low concentrations (5 to 10 p.p.m.) so that symptoms of eye irritation with photophobia and lachrymation occur at an early stage. These symptoms may disappear without treatment and if the worker remains in contaminated atmospheres he is very likely to develop a severe conjunctivitis often after a latent interval of a few hours.

Case 11.—This man, aged 25, was employed in a laboratory where a bottle containing methyl α chloracrylate was accidentally broken on the floor. The laboratory was cleared but the patient proceeded to mop up the liquid with the assistance of one other colleague. He stated that afterwards he washed his hands thoroughly and had his eyes irrigated before continuing to work in the vicinity of the accident. Later that evening he developed the typical eye symptoms described above and the following morning he telephoned the medical department to state that he could not open his eyelids. He was brought to the ambulance room and on examination was found to have a severe bilateral conjunctivitis with oedema of the eyelids and intense blepharospasm. Following prolonged irrigation which was continued in the ambulance he was transferred to hospital where he

Fig. 3.—Facial oedema after the patient was splashed with chloracrylic acid. His normal features are shown for comparison.

Polymethyl Chloracrylate

As has been stated above methyl chloracrylate can be polymerized under certain circumstances to produce a material resembling "perspex". The presence of free monomer or decomposition products under particular conditions is suggested by the fact that machining the polymer on a lathe has given off the typical odour of the monomer and in these two cases has produced eye symptoms. Local exhaust ventilation is sufficient to remove this [illegible]

Chloracrylic Acid

A substance resembling methyl chloracrylate in its properties is α chloracrylic acid, and experimental evidence of its effects is given in Appendix *c*.

Case 14.—This man, aged 22, was employed in the process of esterifying ethylene glycol with chloracrylic acid. The contents of the flask suddenly splashed his face. He immediately irrigated himself with water and subseqently with a dilute solution of potassium permanganate before reporting to the ambulance room. On examination he was found to have first degree burns of the face and neck with a mild conjunctivitis of the eyes. Prolonged irrigation of the eye and the application of a bland cream to the face seemed to produce considerable improvement but by the next day the patient's face had become oedematous (Fig. 3). He also had second degree burns of the interdigital areas of the left hand and on both forearms. The right eye was not inflamed but the cornea showed a central pin head opacity and he was admitted to hospital for further treatment. His condition improved sufficiently rapidly for him to be discharged within a few days. A fortnight after the accident he was seen by an ophthalmologist who reported as follows:

"The cornea shows a near central pin head leucoma which has scarred the anterior epithelium and Bowmans membrane only. It has healed. Near it there are seven or eight minute staining specks on the surface of the anterior epithelium. This will heal without scarring."

On his recommendation the patient continued to have treatment in the form of sulphacetamide drops three times daily for a further brief period. The burns on the hand and forearms were dressed daily until they had healed.

The illustration of this patient's face might well represent the acute effects of formaldehyde vapour with the possible exception that in the latter condition the blisters tend to be smaller and more like eczematous vesicles.

Laminated Plastics

These are plastic materials made by impregnating layers of fabric or paper with resins which are subsequently polymerized by heat and pressure.

... toxicity to be given careful consideration. ... their uses in surgery have already been ... but a few examples are given below of the ... which they may come into contact with food ... drink. Plastics for this purpose may be used in ... of (*a*) cups, beakers, plates, trays, bowls and ... utensils; (*b*) tubes for conveying consumable ... e.g. water, beer, etc.; (*c*) films for wrapping; ... for food containers, refrigerators, conveyor ... and machines used in the manufacture of food.

Plastics used for the above purposes therefore should ideally contain no toxic substance of any kind although this may sometimes be difficult to ensure in practice. In all cases of doubt it is essential that the plastic and its ingredients should be subjected to most rigid physical, chemical, and physiological tests to ensure the absence of toxicity in applications of this kind.

SUMMARY

Synthetic plastic materials are made from polymerized chemicals with the addition of various other compounds.

Polymers can be divided into condensation and addition, or thermoplastic and thermosetting types.

The condensation polymers are typically represented by a group of formaldehyde products. The effects of formaldehyde on the skin and after absorption are discussed. Clinical examples and the incidence of dermatitis in one small factory are quoted. The result of an investigation on workers making formaldehyde products is described to support the contention that formaldehyde has little or no chronic effects when repeatedly absorbed in small quantities.

The nylon polymers are briefly mentioned.

The pathological effects of some addition polymers, their monomers and substances associated with their manufacture are discussed, including polythene, polyvinyl chloride, polymethacrylate, and polymethyl chloracrylate.

A brief reference is made to laminated plastics.

The importance of a full investigation of plastic materials likely to be used for certain purposes is stressed.

I am grateful to Dr. R. G. Heyes for his assistance especially on the chemistry of the polymers: to Dr. M. W. Goldblatt for toxicological reports: to Dr. J. W. Rammell and Dr. J. S. Gourlay for their ophthalmic reports: to Dr. C. H. Hilliard and Dr. V. Magee for their respective opinions on the results of the chest radiographs and blood examinations in the investigation on formaldehyde workers.

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APPENDIX

The following toxicological data were obtained from experiments carried out at the Industrial Hygiene Research Laboratories of Imperial Chemical Industries Limited.

(*a*) **Dinonyl Phthalate** / **Dioctyl Phthalates.**—Each compound used separately gave the following results:—

Oral Administration.—No ill effects observed in