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INDUSTRIAL HYGIENE CONSIDERATIONS IN THE MANUFACTURE
OF REINFORCED PLASTICS

by

William R. Bradley, American Cyanamid Co.

Some 250 years ago, an Italian physician, Ramazzini¹⁰ by name, made observations on the occupations of men to learn if some factor in their work could be associated with the illness and disease that he observed in them. He wondered why those who worked in certain mines lived such short lives after beginning their employment and succumbed to diseases for which there was no cure. He discovered that only slaves and prisoners could be pressed into this type of work, for death was certain after only a few years of labor. He entered one of these mines and experienced the foul air which he felt played some part in disease, not knowing that poisonous gases really existed which, together with various harmful dusts quickly sapped the strength and energies of the workers.

From here, Ramazzini visited the chemist's shop and found him laboring in his smoke and fume filled quarters, breathing the mists and vapors of his many concoctions. At the bleaching pit, the workmen disappeared in the hot gases and mists as they bent over the sulfur vats. And so it went from occupation to occupation. Ramazzini found disease and sickness associated with the conditions of work. But his recorded observations went unheeded by his colleagues, as well as by those who followed.

So it was, that in the early industrial development in this country, men were exposed to gases, mists, fume, vapors, dusts, excessive heat and cold, and excessive noise, with little regard to the possible injurious nature of a number of these substances. In some instances, even though it was observed that life was shortened and that others became physically unfit for further employment in the space of only a few years, there was little attention given as to why these things were so. In fact, in some instances, exposure to harmful and irritant substances was accepted as an unavoidable, although disagreeable, condition of employment. Industrial illnesses, like phosphorous poisoning, mercury poisoning, silicosis from free silica dust in the lungs, and manganese poisoning for years went undetected and unassociated with employment.

Only in comparatively recent years, has there come the understanding that certain industrially used substances may be toxic or harmful if they are permitted to exist as atmospheric contaminants in work places, or if employees are sub-

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jected to physical contact with them. It was also realized that harmful substances might enter the body through the lungs and be absorbed into the blood stream or might be absorbed through the skin, as well as be taken by mouth. With this understanding, came the diagnosis and treatment of illness by industrial physicians and the recognition, evaluation and control of toxic substances in the working environments by industrial hygienists. Today in certain of our larger industries, these individuals, working as teams and together with others have undertaken the study of raw materials, intermediates and finished products in small animal laboratories to investigate their toxic properties.

Even though such studies have been under way for several years, toxicologists are the first to say, "we have only made a beginning." The study of lead poisoning has been continuing for more than 20 years, but a great deal more must be learned before it may be written off as finished. Toxicologists have classified dusts, for example, into those that are harmful and those that are inert, when breathed into the lungs. They have also learned that only the tiniest of particles, those less than 1/25000 of an inch in diameter, too small to be seen with the unaided eye, can penetrate deeply into the air sacs of the lungs. Their studies have revealed the volatile solvents that are harmful whether inhaled or absorbed into the skin, and also just how they produce illness within the body. The studies assume greater importance today in the roll of preventing illness among industries' workmen, particularly in light of investigating the new and useful chemical substances that today are entering the industrial market. One may quickly list those new chemicals useful to the Reinforced Plastics Industry that were unknown only a few years ago; yet, without which there would be no plastics industry. Even now Industrial Physicians are adding to their knowledge in the diagnosis and treatment of illness in men employed in the Plastics Industry and in recognizing and pointing out the difference between illness resulting from their employment and that from non-industrial causes. For not all sickness can be laid at industry's doorstep; in fact, the greater proportion of ill health among those industrially employed is considered due to non-industrial causes.

THE INDUSTRIAL HYGIENIST AT WORK

Industrial Hygienists, frequently, rather arbitrarily, have established certain maximum limits on the concentration of harmful air-borne contaminants that are permitted to exist in the working environment, below which limits it is not anticipated that occupational illness will occur. However, these protective limits apply to a relatively few of our commonly used industrial materials. Yet, even though the entire field of Industrial Health may be considered as comparatively young, much progress has been made; the health of the employee in industry today is tremendously improved over that of a few short years ago. In fact, it is generally agreed that engineering control methods may be used in industry so that even highly toxic substances may be handled safely and without exposure of employees, and that occupational illness is preventable.

There is the challenge for Industrial Hygienists to make concentrated study of the comparatively new Reinforced Plastics Industry. They are interested in studying and classifying the raw materials of this industry and to designate which must be handled with care. With their air sampling instruments, they can measure and ana-

lyze the concentration of gases, vapors, mists and dusts, and recognize, and evaluate the presence and amount of air contaminants that might exist. If nuisance or harmful substances are present, they are concerned that mechanical exhaust ventilation be provided with hooded enclosures at places where dusts and mists and vapors might escape to the workroom air. Applying engineering control measures to carry away and to trap these substances from the standpoint of preventing ill health is their specialized field. When studying how materials are handled, they can determine just where and how a worker may be exposed and can show where personal protective equipment such as gloves, aprons, shoes, clothing or respirators, and face masks may prevent contact with irritant substances.

Transporting solvents by pump through closed systems from storage to the reaction process will prevent the exposure to splashing and to inhaling vapor that would exist if the solvent were carried in open pails or by other open handling methods. Pumping through a closed system of piping may also speed production and lessen its cost. There is always something gained by the careful application of Industrial Hygiene practices.

THE DERMATITIS MYSTERY

In one industry, not long ago there occurred a mysterious episode of dermatitis. In looking for the cause of this difficulty, the plant management were unsuccessful in finding any sign of the offender. Some thought it might be poison ivy, due to its occurrence in the early summer, but this proved not to be the case. Various insects were also suspected of producing this skin rash. Although the plant area involved in this difficulty was a dusty place in which to work, no such affliction had occurred in the past. It is true there had been a case of skin rash here and there, but this time nearly everyone in the building was having trouble. In fact, production had fallen so much that the management were concerned about meeting their commitments on sales. The employees, too, were very much concerned and some were considering seeking employment elsewhere, to get away from the mysterious skin trouble.

The investigation made by the Industrial Hygienist called into the picture supported the early findings of the plant management, but in routine checking and analyzing raw materials, he found that a new and improved ingredient had been added to a powdered product by the supplier. Contacting the supplier, it was learned that there was no information whatsoever on the toxicity of this newly added ingredient, nor was there any indication on the label accompanying the product that a new ingredient had been added. The material at an early step in the process was dried in a small rotary kiln, from which there escaped rather sizeable amounts of fine dust particles that dispersed to the entire work area of the building. This situation was revealed by the Industrial Hygienist's dust counting and air sampling technique, and in further study, his findings ruled out any possibility of other causes of this difficulty.

It is true that no adequate washing or shower facilities were available for the men, and this dust was entering their work clothes which they wore from the plant to their homes. Here, then, was a continuing source of skin contact that pointed to the cause of the dermatitis.

A hooded enclosure was designed for the feed end and discharge end of this small kiln. Exhaust ventilation was applied to these hoods. The dust that formerly had been air borne throughout the plant was now transported to a dust collector where most of it was trapped in large cloth bags. The space around these bags was in turn enclosed and the excess air discharged to the outdoors. New toilet and wash-room facilities were also provided.

As a result of all this, the dermatitis rapidly cleared, the plant area became a much more desirable place in which to work, due to the absence of airborne dust, the employees were very much pleased with the turn of events, and the management was again able to breathe easier. The product trapped in the dust collector was salvaged in such quantities that the ventilation installation paid for itself within a period of six months. Later, the suppliers of this new added ingredient learned to their dismay that they had marketed a product highly irritant to the skin, without indication to the customers through caution labeling.

TROUBLE WITHOUT WARNING

Another episode deals with solvent handling: One afternoon, the Industrial Hygienist's telephone rang and a rather excited voice on the other end of the line unfolded the story of sudden illness on the part of employees, severe enough to result in the hospitalization of a few. The Industrial Hygienist went right over to the plant with his air sampling instruments. After studying the process, analytical measurements showed the concentration of a particular solvent vapor in the workroom to be excessively high. The vapor, although tolerable, quite likely could have caused the sickness. The investigation disclosed that a raw material required dissolving and thinning. It was known that this particular solvent would do the job. Accordingly, the material was put in an open kettle and the solvent added, but the reaction did not proceed very rapidly, and to speed the process, it was decided to install steam coils in the tank and apply heat. The application of heat did the trick, but at the same time released excessive quantities of solvent vapor into the workroom air. The episode of illness and the stopping of production was of grave concern to all. However, the Industrial Hygienist, from his experience, recommended putting a cover on the top of the kettle, installing a manhole with a small hood enclosure, through which materials could be added with safety, and using mechanical exhaust ventilation from the kettle and the manhole hood. The cover was neatly fitted around the shaft of the agitator and the exhausted air was discharged to the outdoors high above the roof of the building. The concentration of solvent vapor rapidly diluted in the outdoor air to the point where it did not create any air pollution problem. Again the plant settled back to work, but in this case, information on the toxicology of the solvent vapor was known and published. How much better it would have been to have had the Industrial Hygienist review the proposed process and apply preventive control measures on the blueprints to be installed at the same time as the process.

TOXICOLOGY OF RAW MATERIALS

The toxicology of some of the raw materials used in the Reinforced Plastics Industry is referred to briefly below. More complete discussions of these and other substances may be found in the industrial hygiene and toxicology texts by Patty⁹ and by Fairhall.²

Styrene is a solvent widely used in the Reinforced Plastics Industry because of its ease of polymerization. The physiological response to the inhalation of styrene vapor and to the contact of styrene vapor with the skin has been published by Rowe,¹¹ by Spencer,¹⁴ and by Carpenter.¹ Absorption of the vapor is mainly through the respiratory tract and in both animals and man, styrene is metabolized and excreted in the urine. Judged from the effect on animals, a maximum concentration of vapor permitted in workroom air has been suggested as 400 parts of vapor per million parts of air. This limit has been suggested for repeated exposures of men for an eight-hour work day. However, the concentration of 400 parts per million may be disagreeable to some persons, and in a few, may cause a transient irritant effect on the eyes and nose. For this reason, the American Conference of Governmental Industrial Hygienists recommend a limit of 200 P.P.M. The sampling and analysis of styrene vapor in the air is easily accomplished, using the method described by Rowe and others. Usually, styrene is handled industrially in closed vessels equipped with positive exhaust ventilation. The use of respirators approved by the United States Bureau of Mines for protection against the inhalation of organic vapors may be useful for short time intermittent exposure to low concentrations of styrene vapor in air.

Diallyl Phthalate has been the subject of investigation by McOmie⁸ and Anderson. They report that diallyl phthalate is a mild irritant to the skin and eyes of rabbits, and that contact with the skin should be avoided, through the use of protective gloves or clothes. Where sufficient diallyl phthalate was introduced into small animals to produce death, sub-lethal poisoning was characteristic by weakness and mild depression. Liver damage and lung congestion were the chief pathological findings. The toxicity of diallyl phthalate is greater than that of other phthalic esters on which data is available. Its greater industrial hazard in the plastic industry is the possibility of chronic illness through long continued and repeated skin absorptions. This points to the desirability of good sanitary facilities for washing and taking showers, the use of rubber gloves when handling the chemical, and for a program of wearing clean work clothing. No maximum permissible exposure concentration has been established for this substance.

Dibutyl phthalate has been reported by Lehmann and Flury⁷ to produce irritation of the mucous membranes, salivation, restlessness and fatigue, with no after effect and with quick recovery in cats, when exposed for 5-1/2 hours to 88 parts of dibutyl phthalate per million parts of air.

The physiological response to vapor exposure of cats to dimethyl phthalate has been reported by the same authors⁷ as giving about the same response when the concentration reached 252 parts per million. It does not seem likely that such a concentration would exist in air mixtures at room temperatures due to its vapor tension.

If dibutyl and dimethyl phthalates are heated or sprayed, control of the work environment to avoid skin contact and inhalation is indicated. No maximum permissible limit of industrial exposure has been established for these compounds.

Tri-o-cresyl phosphate exists in three isomeric forms which possess differences in toxicity. The ortho and metacresyl phosphates are colorless, practically odor-

less liquids which are stable and non-volatile. The paraisomer exists in the form of crystalline needles. Insoluble in water, these phosphates are miscible with the common solvents and thinners and with many vegetable oils. The experimental work by Smith¹³ showed that toxicologically tri-o-cresyl phosphate differs from the corresponding cresols, phenols, or their phosphoric acid esters because following cutaneous or intravenous injections in a dog or cat, a flaccid paralysis of the posterior extremities and to a lesser degree of the anterior extremities occurs after a latent interval varying from five to thirty days. This delayed action of tri-o-cresyl phosphate in the animal body and its specific effect on nerve tissues is interesting. There exists reports in the literature of flaccid paralysis of the upper and lower extremities in persons who have taken tri-o-cresyl phosphate by mouth as an adulterant in salad oil and fat substitutes. Slow but complete recovery is reported to have occurred. One does not anticipate difficulty in handling tri-o-cresyl phosphate in the plastics industry, but the opportunity of contaminating food stuffs or lunches that may be carried into the working area of plants should be recognized. No industrial toxications have been reported; however, the spraying of tri-o-cresyl phosphate or volatilization by heat should be carefully controlled, as absorption of the compound through the intact skin has been demonstrated. Hodge⁴ and Sterner have made further contributions to the toxicological literature on this compound, and methods of detection and determination have been reported by Jacobs.⁵ No maximum permissible limit for industrial atmospheres has been established for this compound.

Benzoyl peroxide is used in the Reinforced Plastics industry as a catalyst because of its effectiveness in bringing about polymerization. In spite of its rather extensive use in the flour milling industry as a bleaching agent, very little investigation on the toxicity of benzoyl peroxide has been made and so far, no injurious effects of industrial importance have been noted. It is known, however, that benzoyl peroxide may inhibit growth in certain plant and animal feeding. Experiments using these plants have indicated a loss of weight. Although benzoyl peroxide possesses a low order of toxicity and no maximum allowable concentration has been set for the presence of this dust in workroom atmospheres, it is considered wise to avoid dust inhalation during handling of this material. The use of dust respirators is suggested to avoid inhalation if the handling technique cannot be made dust free.

The drying agents such as naphthenates or petroleum naphtha have a defatting action following contact with the skin. In the event of possible skin contact, therefore, the use of rubber gloves is indicated. The added metals such as cobalt are usually present in very small quantities. There is no published information on the toxicology of cobalt naphthenate as such from the standpoint of the vapor inhalation, nor has any maximum permissible limit of exposure been established.

Of the materials commonly used as fillers, silica, in the form of silica flour, should receive special attention. Since ancient times, it has been thought that certain dusts caused disease of the lungs; in fact, the writings of Ramazzini¹⁰ discusses it. Illness occurred among tradesmen whose work was in "hewing marble or stones out of rock and in polishing and cutting them." He recognized that the inhalation of dust in some way was related to the condition of the lungs of these persons when seen in autopsy. It is not surprising to find silica exposures in in-

dustry, since the bulk of the earth's crust is siliceous material. There is a great quantity of animal experimentation referred to by Patty⁹ and by Fairhall² showing that the inhalation of free silica (SiO_2) causes a fibrotic disease of the lungs following a massive invasion of the pulmonary tissue. The production of silicosis depends upon the composition of inhaled dust, the number of particles of inhaled dust, the size of the particles, and the length of time during which particles are inhaled. Workmen handling free silica should avoid creating and inhaling dust. Dusty processes should be equipped with exhaust ventilation to prohibit free silica from escaping to the workroom atmosphere. In the absence of such environmental control, workmen should use respiratory equipment approved by the United States Bureau of Mines¹⁶ for protection against the inhalation of toxic dust.

Asbestos in finely divided particulate form is capable of entering the lungs by inhalation. While asbestos is a hydrated magnesium silicate and contains little or no free silica, Lanza⁶ concludes from his study that prolonged exposure to asbestos dust may cause pulmonary fibrosis, termed asbestosis. The production of silicosis is apparently much more rapid than the production of asbestosis, but again the disease depends upon the quantity of dust that is inhaled. Report of a comprehensive study of asbestosis has recently been made by Vorwald¹⁷ et al.

It has been recommended that the maximum permissible limit for free silica dusts and for asbestos dusts in the working environment be 5 million particles of dust per cubic foot of air for eight-hour daily exposure. The Industrial Hygienist employs a special technique of atmospheric sampling and actual dust particle counting, using a microscope in order to make determinations of atmospheric dust concentrations. The figure of 5 million dust particles may be compared with the permissible limit of 50 million particles per cubic foot of air for dusts of the inert or nuisance type, those not considered generally to be productive of fibrosis in pulmonary tissue.

The clays that may be used as fillers are mainly silicates and contain relatively small amounts of free silica, usually less than 5 % and are classified as nuisance dusts, having a permissible limit for atmospheric dustiness of 50 million particles per cubic foot of air.

Fiberglas used in the Reinforced Plastics Industry has been a subject of considerable investigation from the standpoint of its effect on those who work with the material. There has been some irritation of the skin in people who handle it, but most of these cases have cleared up rapidly and the workmen apparently suffered very little further discomfort. The manufacturers of glass wool substances suggest that workers wear clothing loose at the neck and wrists. More important is the recommendation that workmen take a thorough shower at the end of their day's work, using plenty of warm water and soap. Soap and water proved most effective in removing particles from the skin. It is also important that the work clothing be frequently laundered and that the workmen change to street clothes at the end of the work day. Gardner³ conducted extensive investigations on the effect of inhaled glass wool and reported that "apparently even the finest textile glass set up as an atmospheric dust is not inhaled in appreciable concentrations and does not produce any dangerous effect upon the lung". For over a year, he exposed experimental animals to high dust concentrations and found very little in the way of air

borne fibers that penetrated deeply into the lung. Siebert¹² has published a very thorough investigation for the manufacturers of fiberglass that includes a study of the men engaged in production where he found no ill health. Sulzberger and Baer have reported on the effects of fiberglass on animal and human skin, concluding that reactions such as "itch", were of a transitory and superficial nature.

Calcium Carbonate dusts are usually considered in the nuisance category, from the standpoint of industrial hygiene. It has been known, however, to produce irritation of moist skin, particularly when workmen are exposed to heavy concentrations, and may be perspiring freely.

HIGHLIGHTS OF PROCESS CONTROL

The industrial Hygiene considerations of various processes in the Reinforced Plastics industry deal with controlling the environment of the working places to prevent the inhalation solvent vapors or dusts and in protecting employees against liquid contact with the skin. Also consideration should be given to the provision of adequate shower and wash rooms and maintaining a high standard of personal worker cleanliness. A program that will pay dividends in a successful operating experience is one of education among employees in the care they exercise in handling chemical substances used in the industry. If resins that enter the plant in drums are added to open mixing kettles and likewise the solvents and catalysts are added to these same kettles, then consideration should be given to providing enclosures for the top of these kettles and using positive mechanical exhaust ventilation to prevent vapors from escaping to the workroom environment. The use of fillers in the form of dusts should be done with care to avoid inhalation of the dusts, particularly those containing free silica or asbestos. Local exhaust ventilation should be established where resins are sprayed on to reinforcing materials. The application of small sheet metal enclosures at the bed of molding machines with the exception of the working face and applied exhaust ventilation laterally to remove solvent vapor has been successful. It has been possible to make this enclosure, adapting the design and construction of the sheet metal so as not to interfere with the operator or his work.

Certain finishing operations are likely to be dusty, such as sawing and grinding, and while these dusts are mainly considered as nuisance problems rather than as a serious health problem, exhaust ventilation applied to saws and grinders, followed by dust collection has been successful in other industries, particularly the wood-working industry. Control of the working environment from the standpoint of maintaining good health among employees costs money, and the benefits in some cases may be intangible. Yet the provision of a good working environment points to continued production, the increased opportunity to produce at a greater rate, and in attracting and holding good workmen in the industry. It has been said that "production comes from people". Providing a clean and healthful place where people may work certainly benefits production.

INDUSTRIAL HYGIENE SERVICES

Where are the services of Industrial Hygiene available? Many states have established bureaus of industrial hygiene within their state department of health or depart-

ment of labor, and these groups are ready to advise industry on problems of the working environment. A few insurance companies staff industrial hygiene personnel who are made available to assist their compensation risks. Several large companies maintain their own industrial hygiene groups. In addition to these people, there are a few private consultants, both as individuals and as groups, in the field of industrial hygiene.

It may be that the Reinforced Plastics Industry would consider the services of a consultant on the subject of industrial hygiene to conduct a survey of a representative number of member organizations of this group. Such a person might well be staffed by the Society of the Plastics Industry. He could ascertain the status of various processes from the standpoint of employee health maintenance, determine where preventive measures may be taken against potential illness and develop advices leading to a continued production with the avoidance of both health and nuisance problems. Of particular value would be consultation with the Industrial Hygienist when new processes or new chemicals are anticipated, so that precautionary provisions for a good work environment can be established well in advance of production. This, then is the challenge for modern industry.

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QUESTION - Presented by Calhoun Shorts, Pacific Plastics Co.

Is the itching caused by glass fibers a mechanical or toxic effect?

ANSWER - By William R. Bradley, American Cyanamid Co.

The so-called itching that has occurred when handling fiber glass under dusty conditions has been shown to be entirely a mechanical effect.

QUESTION - Presented by William Cruse, The Society of the Plastics Industry

Are you familiar with a bill now before Congress which will prohibit the use of certain chemicals in the food processing industries?

ANSWER - By William R. Bradley

I am not familiar with details of such a proposal. However, it would seem to be more a question of residual concentration of chemicals to be permitted rather than outlawing certain chemicals in the food processing industries. The human body is such a complex chemical plant that arbitrarily prohibiting use of chemicals without sufficient toxicological study would be unwise.

QUESTION - Presented by Robert B. White, Laminated Plastics, Inc.

Is there any danger from inhaling styrene fumes?

ANSWER - By William R. Bradley

Styrene vapor may be inhaled in concentration up to 400 p.p.m. for long periods of time without much opportunity for harm. Styrene, when absorbed in the blood, is rapidly detoxified.

QUESTION - Presented by F. H. Humphrey, Fleet Fiberlast, Ltd.

(1) Can cases of dermatitis be caused by monomeric styrene? (2) Can you recommend a specific type of skin cream?

ANSWER - By William R. Bradley

(1) Styrene can cause dermatitis following promiscuous use and handling that would involve continued contact with the skin. Styrene may remove the natural fat of the skin. (2) Water-insoluble type creams.

QUESTION - Presented by James Lunn, Lunn Laminates

From the standpoint of industrial hygiene, what are the most serious problems to consider in the field of Reinforced Plastics?

ANSWER - By William R. Bradley

In my opinion the most serious health exposure problem in the Reinforced Plastics industry is the opportunity for intermittent inhalation of toxic dusts and vapors.