IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

Several methods have been developed for determination of isocyanates in air. In the Ranta method described by Zapp, [48] the sample is collected by passing air through a bubbler containing aqueous sodium nitrite and ethylene glycol monoethyl ether (cellosolve). TDI that is present results in the formation of a yellow-orange color, the density of which is read in a photoelectric colorimeter, using a 450 nm filter, and comparing against standards containing known amounts of TDI. This method measures both TDI and TDI urea, the latter being formed in moist air. In the Marcali method, [58] TDI is hydrolyzed to an amine by bubbling the sampled air through a dilute mixture of acetic and hydrochloric acids. The amine is diazotized and coupled with N-1-naphthylethylenediamine. The reddish-blue color produced is measured spectrophotometrically at 550 nm.

There are commercially available field kits employing modifications [64] of the Marcali method. While very useful for routine monitoring, the lowest concentration measurable with their present color standards is 0.01 ppm. If the kits can be improved to accurately measure 0.005 ppm, they should be acceptable to meet the monitoring requirements of the standard.

In England, Reilly [65] developed a test paper method reported to require less analytical skill than the Marcali method. The intensity of a stain produced by TDI on a treated paper is compared

with artificial standards. A continuous monitoring unit has since been developed [66] in which a tape of the treated test paper, through which the sampled air is drawn, is monitored by a lamp and photocell. The signal from the photocell is amplified and used to drive a readout meter and an alarm system operating at a preset level, usually 0.02 ppm. A recorder can also be connected to the monitor. The sensitivity of this continuous monitor was not reported, [66] but the lowest readout point (above zero) is 0.01 ppm.

Belisle [67] has described a field kit employing another method which involves drawing the air sample through an acidified absorber solution in a modified midget impinger containing beads of an ion-exchange resin and glutaconic aldehyde. The color which develops on the resin beads is matched against color standards. Results are reported to check closely with those obtained by the Marcali method.

Other methods or modifications of the Marcali method have been developed. [64,68,70,71] However, the Marcali method, [58] with some modifications, is presently the recommended method, because of its demonstrated reliability and wide use. Most of the information about the health effects of TDI, as well as its environmental control, is related to data obtained by the Marcali method.

The value of a reliable recording continuous monitoring system for TDI is self-evident. If the tests under in-plant situations show good correlations between the new continuous tape monitor [66] and the Marcali method, and adequate sensitivity, use of the monitor should be encouraged.

A gas chromatographic method has recently been developed [72] that is claimed to give much greater sensitivity than existing methods (ER Hermann, written communication, April 1973). If subsequent evaluation bears this out, this method, or a modification thereof, may prove to be a much better method for analyzing airborne TDI, and may resolve the present difficulties in detecting brief excursions of TDI, believed to be of toxicological importance, and still allow sensitive detection of TDI concentrations below the recommended time-weighted average.

Control of Exposures

The engineering control of TDI vapors is, in theory, clear-cut, since the application of established principles of exhaust ventilation will remove them from the work environment. However, although the techniques have been known for a number of years, they are not as widely used as they should be. [73] In practice, these principles are feasible to apply in many, but not all situations in which TDI exposures occur. The data shown in Table XIII-2 testify to the feasibility of controlling levels within the recommended limits. [49] In fixed locations most operations may be successfully enclosed or hooded, with ventilation face velocities of the order of 200 feet per minute being adequate to control vapor concentrations. [14]

There are a vast number of polyurethane products, and there are a great many uses for polyurethanes, some of which require that they be formed in the field under circumstances where the use of conventional exhaust ventilation procedures is difficult. A variety

of operations may be involved, in the field as well as in fixed locations. These include spraying, mixing, foaming, injection, flushing, pouring-in-place, and painting. Many operations require few people; some involve teams consisting of only two or three workers, some possibly even one. Even where exhaust ventilation is feasible for vapor control, operations such as spraying produce high concentrations of isocyanate mist. [74] Adequate protection in such cases requires exposed workers to have the supplementary protection of positive pressure supplied air respirators. [1]

In employing exhaust ventilation for the control of TDI, the design principles presented in Industrial Ventilation - Manual of Recommended Practice, [75] published by the American Conference of Governmental Industrial Hygienists, and Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2-1971, [76] published by the American National Standards Institute, should be followed. Recirculation of exhaust air within the workplace should be prohibited. The exhaust air should be scrubbed before discharge.

Scrupulous housekeeping, with immediate cleanup of spills, removal of all scrap, and proper closure and storage of containers of TDI is of paramount importance. Any large quantity of TDI that is to be disposed of should first be transformed into a urea, by reacting with water, to which a small amount of isopropyl alcohol and ammonia may be added. [2,14] Poor maintenance of equipment and facilities can negate the usefulness of expensive exhaust and general ventilation.

If a satisfactory product can be made, the degree of isocyanate exposure can be markedly reduced by substitution of a less volatile isocyanate compound, such as diphenylmethane diisocyanate (MDI) or a polymeric isocyanate. [77] Because of its lower vapor pressure, MDI concentrations in air will not normally be high enough to cause marked toxic effects, unless the temperatures are significantly raised. However, reactions involved in producing urethanes are exothermic. [17] Thus, elevated temperatures may cause an increase in airborne diisocyanate.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

An environmental limit of 0.1 ppm was first proposed as a tentative value, according to Elkins, [49] by Ascue in 1954 on the basis of animal experiments at the Haskell Laboratory and later published by Zapp. [48] The same figure was endorsed by Zapp, in his 1957 paper, [48] and based on the respiratory tract irritation of animals at concentrations of 1 to 2 ppm TDI, employing an arbitrary safety margin of 10- to 20-fold. The analytical method employed in the studies on which these recommendations were based was that of Ranta as described by Zapp. [48]

According to Elkins et al [49], the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) adopted 0.1 ppm as a tentative Threshold Limit Value (TLV) in 1956 and as a recommended value in 1959 largely on the basis of Zapp's animal work.

However, reports of adverse effects (respiratory sensitization and asthma-like phenomena) found in a number of work populations in different countries continued even though a TLV of 0.1 ppm had been observed. This and the work of Elkins and co-workers [49] influenced the Threshold Limits Committee of the ACGIH to reduce the TLV to 0.02 ppm in 1961. [78] Elkins et al [49] in fact had recommended a reduction to 0.01 ppm which has been followed as the standard in Massachusetts. In 1962 the reduction to 0.02 ppm was endorsed by Henschler et al [55] who had repeated Zapp's original animal studies

and found very similar results but at 1/10 of the exposure levels published by Zapp. [48] The discrepancy was attributed to the different analytical methods used for TDI.

The ACGIH still recommends a TLV of 0.02 [78] which is a "ceiling" value, not to be exceeded. Although the Committee acknowledged the reports of Peters and his group [39-44] on acute and chronic effects observed in workers apparently not exposed to levels as high as 0.02 ppm, they did not consider these changes to be of sufficient importance to invalidate this TLV.

In 1959 Smelyanskiy and Ulanova [79] of the U.S.S.R. published the maximum permissible level (ie a ceiling value) of TDI as 0.07 ppm. This is noteworthy because Soviet MAC's tend to be very much lower than ACGIH recommendations. This figure was only slightly lower than the ACGIH TLV for the same year, and is three and a half times higher than the ACGIH limits from 1961 to the present time. Their report [79] listed permissible levels of many substances and did not report the basis for the TDI level.

The current Federal Standard (see 29CFR 1910.93), a ceiling value of 0.02 ppm, is based on the ACGIH recommendation. It is published in the Federal Register,Volume 37, Number 202, page 22141, dated October 18, 1972.

Basis for Recommended Environmental Standard

There is reason to believe from the recent studies of Scheel [80] that cases of sensitization continue to occur. Whether such sensitization takes place at levels of exposure to TDI at or below a

time-weighted average of 0.02 ppm or during brief excursions to higher levels following accidental spillage [51] cannot be determined from the available data because in no case has continuous monitoring of TDI air levels been reported. Some authors [20,25] believe that preplacement screening and exclusion of employees with a personal or family history of clinical allergy or atopy largely eliminates the problem of sensitization to TDI in industry. Even if this were the case, such an approach is not consistent with the current objective of a standard to protect all workers. Moreover there is at least some suggestion that TDI may be a universal sensitizer. [63]

A different kind of problem is raised by the findings of Peters and his co-workers [39,41,44] in New England which are to some extent corroborated by Adams [45] in Britain. (These studies are discussed in some detail under the heading of Epidemiologic Studies in Section III.) Peters has been studying a dwindling cohort of workers, originally 38 in number but reduced by loss to follow-up to 13, since 1966. Working in a plant producing polyurethane foam by a continuous process, in which air levels of TDI had never been found to exceed 0.014 ppm, Peters and his coileagues have found acute reductions of ventilatory capacity (FEV 1.0) in workers at the afternoon (end-of-shift) measurement compared to the morning (pre-shift) measurement. These acute changes were not completely reversed overnight; cumulative changes exceeding by 3- to 4-fold those associated with age alone have occurred over periods of 6, 12, 18, and 24 months; symptomatic workers showed a greater response to TDI than asymptomatic ones; and a

substantial positive correlation existed between the acute and cumulative changes in FEV 1.0. In the published papers cited, [39-44] all the physiological data from individual workers have been pooled and expressed as group mean values. Moreover, the published environmental data in these studies are sparse. However, the nature of the continuous pouring process and of the plant is such that spillages and their attendant excursions are less likely than in some other operations. The only level of TDI at which Peters [42] recorded a minimal diurnal decrement in FEV 1.0 (a mean decrease of only 0.05 liters in 43 workers) was very low, with a maximum concentration of only 0.0015 ppm. The findings of Peters and his colleagues can be challenged on the grounds that they failed to detect significant excursions that might have occurred; thus, the implications of Peters' findings in the development of a standard are difficult to interpret except as probably indicative that the standard of 0.02 ppm is too high, and that the limit recommended in the 1962 report of Elkins et al [49] of 0.01 ppm may also be too high.

Peters' results, although inconsistent with the negative findings of insignificant diurnal changes in FEV 1.0 in 18 TDI workers exposed to higher levels, [51] were presaged by those of Gandevia [38] who found a group mean diurnal decrease of FEV 1.0 of 0.18 liters in 15 workers exposed to substantially higher levels of TDI (estimated at 0.9 ppm), and are corroborated by more recent studies by Adams [45] who has been following, spirometrically, more than 100 TDI workers in Britain for five years. In this last study TDI air levels appear to

have exceeded those which Peters found but "rarely exceed 0.02 ppm." [45]

It appears therefore that a time-weighted average standard of 0.02 ppm TDI is too high to prevent the acute and cumulative decreases in ventilatory capacity, measured by FEV 1.0, as reported by Peters and Adams.

At the same time, a reduction of the standard to the level at which Peters reported only minimal effects, ie 0.0015 ppm, does not seem to have sufficient justification. The majority of the workers in Peters' [39-44] and Adams' [45] studies appeared to be asymptomatic and it is possible that the effects were caused by brief, unrecorded excursions, or that insufficient samples were collected to define the environmental exposures. The long-term health effects of the observed accelerated decrement in ventilatory capacity, as reflected by the FEV 1.0, are not known, nor is it known whether these effects may be reversible on removal from exposure. [45]

With consideration to the limitations imposed by data both conflicting and lacking in important detail, it is concluded that protection of the worker not yet sensitized to TDI can best be achieved by adherence to both a ceiling limit and a time-weighted average limit. The data on which the ACGIH TLV, and thus the Federal Standard, of 0.02 ppm was based were from the report of Elkins and co-workers. [49] They had recommended a lower value, 0.01 ppm, to the ACGIH in 1961, and their subsequently published data [49] justified a value lower than 0.02 ppm.

After a review of these and other quantitative data relating exposure to effect, it is concluded that these data still offer the best basis for recommending a time-weighted average limit, and give some, but limited, support for the recommended ceiling limit. The summary table from the report of Elkins et al, [49] shown in Table XIII-2 primarily because of its information on average environmental levels, can be misleading in trying to relate TDI effects with environmental levels, because the concentrations listed are often averages over a long period, up to several years, whereas the effects noted occurred over a small part of that period at a different exposure level, described in the text of the report and in other tables. Data relevant to the present discussion have been taken from that report after careful study of all tables and textual discussion, and are summarized in Table V-1. In the early phases of this study, the Ranta method [48] was used for analysis, but later the Marcali method [58] was adopted in its place. The authors compared the two methods, and reported that they gave reasonable agreement, but preferred the Marcali method because of its greater sensitivity.

Data from the report that the authors felt to be of doubtful validity were excluded from Table V-1, as were some data which do not allow comparison of concentration and response. It was not possible in most cases to glean from this report an accurate estimate of the number of workers exposed, and the number in the column listing the maximum number of workers at risk is probably higher than the true number at risk in most cases.

From these data, it can be seen that at all exposure levels of 0.01 ppm or higher, some cases of TDI toxicity occurred, but there were no cases at 0.007 or lower. At 0.009 ppm, there were no established cases, but one questionable one; there were several established cases at 0.008 ppm. It is concluded that the time-weighted average environmental limit should be below 0.01 ppm, and should be 0.005 ppm to ensure some margin of safety.

A ceiling of 0.02 ppm is interpretable from several studies, such as that of Williamson, [33] who believed cases of sensitization occurred only when spills resulted in excursions over 0.02 ppm. Some of the data of Elkins and co-workers [49] could be interpreted to support such a ceiling, if, as seems likely, the workers in plant 3 in the 1958 survey (see Table V-1) who wore respirators did so because of the acute response to levels around 0.02 ppm. But the data which better support a ceiling are those of Hama, [15] who found no evidence of toxic effects by TDI when the environmental level was under 0.03 ppm. The airborne TDI level had been about 0.01 ppm, with no complaints, when an operational change resulted in an increase in TDI levels, to a range of 0.03 to 0.07 ppm; all 12 workers were then adversely affected. When hygiene was improved, airborne TDI was reduced to between 0.01 and 0.03 ppm. Over a period of several months at this level, no worker suffered from TDI effects. From this a ceiling limit of 0.03 can be interpreted. A limit of 0.02 ppm is nevertheless recommended, in part because of the long sampling time (20 minutes) dictated by the lack of sensitivity of the Marcali

Table V-1

Summary of Dose-Response Data of Elkins et al [49]

Plant	Date	No. of Tests	Concentration, ppm Max.	Concentration, ppm Av.	No. of workers affected: Estab-lished	No. of workers affected: Question-able	Max. No. at risk	Notes
2	1/58	8	0.01	0.008	3		50	
2	12/58	6	<0.01	0.005	0	0	50	
2	12/60	6	0.05	0.04	14	25	100	(1)
2	1/61	9	0.03	0.01				
2	6/61	6	0.02	0.008	3	2	50	
2	1/62	6	0.014	0.008				
3	1958	4	0.02	0.01	0	0	25	(2)
3	1961	8	0.015	0.007	0	0	25	
4	1959	4	0.02	0.01	1	3	40	
4	1961	5	0.001	0.0006	0	0	40	
4	1961	0			4			
5	1959	4	0.02	0.015	?	?	6	(3)
6	1961	28	0.07	0.015	3	0	40	
9	1961	3	0.008	0.006	0	0	4	
12	1962	6		0.009	0	1	6	
13	1962	4		Nil	0	1	20	
14	1962	6		0.000	0	0	20	

Notes:

(1) Additional company analyses verify that air levels were high.

(2) The workers wore respirators, which probably indicates acute irritation.

(3) Some workers had been transferred after complaints.

method. [58] A 20-minute sampling time is barely adequate for adherence to the recommended TWA, and any reduction for testing compliance with ceiling values will preclude checking compliance with TWA's. Thus, the limits and many of the data from which they are derived represent a compromise resulting in part from the lack of optimal sensitivity of the analytical method.

If only a small part of the working population is sensitizable to TDI, as believed by some investigators, [25,31] it could be inferred that the ceiling that protects against acute irritation in most workers also protects against sensitization in a few. But the available data do not allow such precision of interpretation.

The use of parts per million (ppm) throughout this document follows convention in treating TDI as a vapor. However, it is possible that TDI may exist in particulate form in some operations. Data on relative toxicities of particulate and vapor-phase TDI are lacking, but it is believed there would be no significant difference in toxicity of the two forms. Large-size particulates may be removed in the upper respiratory tract, and thus not reach the bronchioles, but they are doubtlessly irritating to the upper respiratory tract, so sampling for selected particle sizes is not proposed. Additionally, the reaction of TDI with upper respiratory tract tissue cannot be ruled out as an initiator of the sensitization reaction. Partially polymerized particles of TDI will probably be less toxic than the monomer, but such particles will be sampled and analyzed as TDI to a lesser degree. From a theoretical point of view, the decrease in

toxicity of TDI with degree of polymerization should parallel the decrease in sensitivity to polymerization of the sampling and analysis. Thus, it is proposed that the environmental limits of 0.005 ppm TWA and 0.02 ppm ceiling also apply to particulate TDI, expressed as 0.036 mg/cu m TWA and 0.14 mg/cu m ceiling.

Available evidence does not point to a level of airborne TDI that is safe for workers already sensitized to TDI. While it can be speculated that there is a dose-response relationship for sensitized individuals, from theoretical considerations and from interpretation of some unpublished observations, there is no substantial evidence either that such a dose-response relationship exists or that points to what a safe concentration for sensitized people is. Thus, the common warning that those sensitized to TDI should not be exposed to the compound at any concentration, and should be removed from work involving possible exposure to TDI, seems sound from present information.

The decrement in respiratory function seen in the studies of Peters et al and of Adams seems consistent with a prediction of the development of obstructive lung disease if such a decrement progresses for a long time. Similarly, repeated asthmatic-like incidents among workers exposed to TDI might be followed by the development of obstructive lung disease. Thus, the medical recommendations include X-rays and pulmonary function tests to try to detect both acute and chronic effects on the respiratory system. It is desirable to perform occasional "before and after" tests of pulmonary function, ie, tests

of function at the beginning of the workday and at the end, to see if there are small but significant changes in an otherwise apparently safe work environment.

A questionnaire to elicit any history of relevant respiratory problems has been found useful in some industries, and may be of value to others. An example of a useful questionnaire, given in Appendix V, is that published by the Health Advisory Committee of the British Rubber Manufacturers' Association [81] for TDI workers.

VI. WORK PRACTICES

Toluene diisocyanate containers should be kept closed as much as possible to prevent the escape of vapors and to prevent water from getting in. When it is necessary to open a container, adequate ventilation should be provided and, in addition, workmen should wear chemical safety goggles and respiratory protective equipment. When it is necessary to pour TDI from a container, a flexible hose leading to the exhaust system should be placed in the container. [2]

When TDI leaks or spills occur only properly protected personnel should remain in the area. Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers. Adequate preparation and facilities for handling spills should be provided. These include suitable floor drainage and ready accessibility of hoses, mops, buckets, and absorbent materials. Spills should be cleaned up promptly. The effectiveness of water is considerably improved by the addition of 1 to 5% of ammonia. This solution is further improved by the addition of up to 10 % of isopropyl alcohol. Oil absorbent materials such as sawdust or vermiculite are also useful in facilitating clean-up of spills. Such material, after use, should be shovelled into an open top steel container, the container then covered and removed to a safe disposal area away from the operating area. The mixture should be soaked with water containing ammonia and allowed to stand for 24 hours in an open or partially open container, after which the container can be closed and discarded. [3,82]

Liquid TDI should never be washed directly down the drain with water, because the solids that result may plug the sewer line. Spills of TDI will freeze during cold weather. In such cases the use of water and ammonia will merely coat the solid material with insoluble urea stopping further reaction. In cold weather clean-up should be performed with a mixture of equal parts of isopropyl alcohol and perchloroethylene. It is advisable to have a supply of this mixture on hand and ready for immediate use for cold weather.

If major spills occur, air-supplied masks or self-contained breathing apparatus must be used by workers in the area.

Unprotected workers should not be permitted within 50 feet of spraying operations performed outdoors. A greater distance is required to protect against drift during indoor spraying operations, the distance being dependent upon the ventilation provided. An air-supplied hood, impervious gloves, tightly buttoned coveralls, and impervious foot covering are needed by all workers within 10 feet of a spray gun in operation, according to Peterson et al. [74]

Employees shall be instructed concerning TDI hazards and the precautions to be followed. They must be trained to report promptly to their supervisors all leaks, suspected failures, exposures to TDI, or symptoms of exposure. The location of safety showers, fountains, and eye baths must be made known to all employees. The importance of good housekeeping should be emphasized and the need for immediate removal of TDI or reacting foams spilled on the skin, by thorough washing with soap and water, should be impressed upon all workers.

The necessity for prompt and thorough flushing of the eyes with water for 15 minutes in the event of contact should also be stressed. If TDI gets into the eyes a physician should also be called. [3]

Cup-type chemical safety goggles should be worn wherever there is danger of liquid TDI coming in contact with the eyes. For normal continuous eye protection, spectacle-type safety glasses with 48-wire mesh side shields may be used. Eye protection equipment should meet the specifications of the Z87.1-1968 standard of the American National Standards Institute. [83] Only respiratory protective equipment specified in Section 4 of this recommended standard should be used. Where supplied air equipment is used, the air supply must be from a source not subject to contamination with TDI. [84] Safety shoes are recommended for workers handling drums of TDI. Rubbers may be worn over leather safety shoes. Rubbers should be thoroughly cleaned and ventilated after contamination. Shoes which have become contaminated with TDI should be decontaminated or cut up and disposed of. [2]

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