Memorandum on the Hygienic Requirements for the Manufacture and Transportation of Ethyl Fluid, and for Mixing Ethyl Fluid with Gasoline.

I. Hygienic Aspects of the Manufacture of Lead Tetraethyl.

The design and construction of buildings and equipment for manufacturing operations is by far the most important factor in determining the degree of safety associated with the manufacture of lead tetraethyl. Other measures of control have been found necessary in order to obtain satisfactory results, but it must be recognized as a first principle that no amount of caution and no amount of medical and hygienic supervision can possibly modify significantly the basic conditions of lead exposure which arise from the character and quality of the equipment. The oily liquid, lead tetraethyl, is sufficiently volatile at ordinary temperatures to cause acute danger of death from its inhalation. It is also capable of fairly rapid absorption through the healthy and unbroken skin, so that all contact with the skin must be avoided. Therefore this material must be kept and handled in closed pipes and containers. This is difficult to accomplish since the liquid tends to creep along a surface with which it is in contact, and if there is the slightest opportunity it escapes from the joints of the pipes, pumps, and storage tanks. The methods of manufacture also involve chemical reactions and separatory processes (distillation, etc.) in which lead tetraethyl occurs in the vapor state, and at times under pressure. In such a state it is even more difficult to prevent leakage. All the equipment employed, such as autoclaves, distilling

be constructed on precise specifications and with the highest quality of workmanship. Pipe-joints must be eliminated by employing welded construction wherever feasible. The only type of pipe-joint that has been found at all satisfactory is a flanged joint, with the flanges welded to the pipe-lengths and bolted together with heavy bolts which can be drawn up tightly, with an intermediate gasket of fairly heavy fabricated sheet asbestos. Sight-glasses, which are absolutely necessary in certain pipe-lines in connection with several operations, are a potential source of significant leakage and must be specially constructed. It has been found feasible and necessary to build a sight-glass of welded metal with small but heavy (1 inch thick, bullet-proof glass) flat windows in the front and back, with the windows drawn up tightly, by bolts, against an asbestos gasket which is also in opposition to an outside metal flange. (The customary type of sight-glass leaks regularly and continuously). Pumps of the customary type are quite unsatisfactory for handling lead tetraethyl, for leakage is absolutely inevitable. A "Lewis" type of pump, in which there is a revolving shaft with a packing gland only at the top which must always be above the liquid level of the material being pumped), is the only type found satisfactory in practice. Because of the slight leakage of vapor at the top of the column local ventilation must be employed so as to carry away all vapors. Autoclaves and stills must be equipped with certain moving parts such as agitators which penetrate their shell. All such vessels, regardless of the excellence of their construction and maintenance, will inevitably leak at stuffing-boxes or packing glands. If badly designed and constructed they will leak profusely. Accordingly every effort must

be made to obtain the best of workmanship in the construction of such vessels. Even so, it is necessary to apply unit ventilation to these pieces of apparatus, to such an extent as to maintain a safe atmosphere around them. This may be done by surrounding them with a comparatively tight booth which is specially ventilated, and which is kept under slightly negative pressure so that no vapors escape from it into the main working space.

All parts of the manufacturing plant in which liquid lead compounds are produced and handled must be carefully ventilated to such degree as is necessary to maintain the atmospheric lead concentration below a toxic level. The lead concentration in any part of the plant should not be permitted to exceed 2 milligrams of lead per 10 cubic meters of air for more than short periods, and the basic concentration of any point should not exceed 1.5 milligrams per 10 cubic meters. The lead concentration in the air should be determined regularly by precise methods of air-sampling and analysis, so that there may be no conjecture as to the actual conditions prevailing in the plant. It has been found that the ventilation to be efficient and uniformly adequate must be operated along the following lines:-

1. Points at which small quantities of vapor escape from equipment regularly or frequently must be locally ventilated by suction to avoid the significant contamination of adjacent areas.

2. Air must be forced into all parts of the building to such an extent as to maintain a slight positive pressure, thereby avoiding the backing up of vapors from drains into which lead tetraethyl may have gone because of leakage or accidental spills. Air must be introduced into individual rooms and working spaces so as to produce

complete changes in proportion to the extent of the lead contamination from apparatus within such spaces.

3. The air introduced into rooms must be balanced to the desired degree by the withdrawal of air by suction fans.

4. Concentrated vapors which regularly escape from operating equipment (such as, for example, in venting the autoclaves or stills) must be removed by accessory exhaust ventilation, and must not be carried by the general ventilating ducts of the building.

5. The most rigorous care must be taken in locating the air intake and exhaust openings so as not to reintroduce exhausted air into the building through the intake lines and so as not to pick up smoke and fume from the furnaces employed to reclaim lead from the residue of the reaction vessels.

6. The residue or "sludge" removed from the reaction vessels must be carried in a closed pipe line to a pit which is completely housed in and which is kept under slightly negative pressure by exhaust ventilation in such manner that the overlying vapors do not escape into the adjacent atmosphere.

Reaction vessels, in which high pressures may develop, must be equipped with vents and also with pressure disks so as to prevent explosions within the building, if and when the reaction procedes at an uncontrollable speed.

Every operation in the manufacture and handling of lead tetraethyl, and in the maintenance and repair of equipment requires skill and training and also expert supervision. The repair operations, the removal of old equipment, and the replacement of new apparatus are especially hazardous. It is highly necessary, therefore, that

care be exercised in the selection of the plant personnel. Complete details of every operation should be worked out and recorded as operating and safety instructions. Precise discipline must be maintained in carrying out such instructions. The men should be fully aware of the dangers of their occupation and should know how to protect themselves against lead absorption at all steps. They need to be warned specifically against certain practices, as for example, opening reaction vessels before complete cooling, and entering such vessels or tanks, regardless of circumstances.

Emergency showers, with water, should be available in all parts of the plant where contact with lead tetraethyl may accidently occur, and a convenient supply of kerosene must always be available so that any lead tetraethyl which may come in contact with the skin can promptly be washed off with this material. Ordinary wash stands with soap must be conveniently situated on each floor, and toilet facilities must also be provided on each floor.

Positive pressure air-line hose masks must be provided for the several operations which otherwise involve unavoidable exposure to lead tetraethyl vapors. Such facilities are required when men must enter the specially ventilated booths surrounding the autoclaves and stills. They must also be used in removing the bags from the bag-filters. No man should be permitted to enter the building surrounding the sludge-pit without using an air-line mask. Certain repair operations which necessitate breaking into a pipe line that has been used to convey lead tetraethyl require such masks.

The ethyl chloride storage and recovery equipment should be housed outside the lead tetraethyl building in a place where fire hazards will not affect the other operations. All pipe connections

must be leak-proof, and tanks and pipes must be thoroughly grounded. Only such quantities of ethyl chloride as are needed to carry on current manufacturing processes should be handled within the lead tetraethyl building.

A complete over-head sprinkler system for fire prevention should be installed in the lead tetraethyl building, except in such areas as may permit contact of the water with sodium or lead sodium alloy. Piping systems and reaction vessels must also be well grounded against static accumulation.

The Alloy Building

In connection with the manufacture of lead tetraethyl there must be facilities for the preparation of a lead-sodium alloy. The sodium used for this purpose, and the alloy which results from the operation, must be protected carefully against water, and consequently pipe lines for water, faucets and hose lines must be kept out of working areas in which these materials are handled. However, there must also be adequate provision for the elimination of dusts and fumes. The pots in which the alloy is prepared must be enclosed in an adequately ventilated booth and there must be completely ventilated booths in which the hot freshly cast alloy can be kept until cooled. Although the alloy is brittle and tends to give rise to but little finely divided dust when broken or gound in a mill, there is need, nevertheless, to prevent exposure to dusts. The floors, therefore, must be kept clean by sweeping with a copious supply of saw-dust impregnated with kerosene, and the mill must be protected against discharge of particles at both the feed and discharge side. Men engaged in removing molten alloy from the pots into the moulds must also wear dust and fume masks of correct design.

Air analyses must be made at various points in the alloy department, and housekeeping must be rigidly supervised to maintain the maximal degree of cleanliness and freedom from hazard.

The Reclamation of Lead from Sludge

The sludge stored in the sludge pit and dryer must be removed mechanically by a bucket or shovel operated by remote control from without the building and introduced into a hopper which will feed it at a proper rate into a properly designed melting furnace. If this equipment is properly designed and operated no vapors of lead tetraethyl will escape into the furnace room. The molten lead withdrawn from such furnace must not be permitted to contaminate the working space with its fumes. The pot from which the lead is ladled, and the casting moulds must be so designed as to be capable of adequate ventilation until the pigs of lead are cooled well below the temperature at which lead is appreciably volatile. This can be done by having a revolving pigging table which permits the newly poured pig to be shifted promptly into a ventilated box from which it emerges cooled at the other end. This table should be in close relationship to the pot from which the molten lead is removed by a ladle or pouring device. This pot also should have a hood over it connected to an exhaust duct.

The Disposal of Plant Wastes

All waste materials from the plant, including waste water from plant operations and that used to wash down floors, together with all lead-bearing materials from reaction vessels, pipe lines and other containers, must be dealt with or diluted in such a way as to prevent the pollution of adjacent soil and streams.

Materials and equipment which are to be discarded should be destroyed, if possible by burning, and should, in any case, be

freed of volatile lead compounds by being burned to a dull red heat in a bonfire under conditions which will not give rise to exposure to fumes and smoke. Slag or equipment contaminated with lead compounds must be buried or so disposed of as to prevent harm to uninformed persons.

II. The Hygienic Problems Associated with the Blending of Lead Tetraethyl with other Ingredients to make Anti-Knock Fluid.

The exposure to lead tetraethyl is of the same type in the blending plant as in the plant in which the lead tetraethyl is manufactured. The finished lead compound must be mixed with other ingredients, of which the most important, from the hygienic point of view, are ethylene dibromide and ethylene dichloride. The latter two compounds are toxic liquids of somewhat higher volatility than lead tetraethyl and they give rise to danger of acute poisoning from inhalation and skin contact. In their acute manifestations these poisonous substances produce narcotic effects, followed by central nervous system irritation and delayed damage to the liver in non-fatal cases, and by collapse and coma in fatal cases.

It is necessary that the blending be carried out with great care and by means of precise equipment, in order to avoid exposure to lead tetraethyl and the organic bromine compounds. Since drums must be filled, the piping system must be open at the point where filling operations are carried out. A filling booth must be constructed in such a way that all vapors are carried away completely, and with control apparatus which is operated entirely from outside the booth. One means for this purpose consists in the

use of a weighing platform of sufficient size to carry the drums, completely enclosed and heavily ventilated, with a glass window through which the filling can be watched. A shallow pit beneath a metal grill should be arranged to catch any accidentally spilled material, and a copious supply of continuously running water should flush away any spilled material promptly.

The toxic liquids should be moved by gravity flow so far as possible but mixture must be accomplished by agitation. Accordingly, the top of mixing tanks must be so ventilated as to prevent leakage of vapors into the rooms from the stuffing box around the agitator shaft. The pumps for handling the liquids should be of the "Lewis" type, ventilated at the top of the column.

The containers for the finished Fluid must be limited as to type and capacity to those which are capable of safe transportation and which are designed for use in authorized and controlled mixing operations. It is of the utmost hygienic importance that irregular procedures for handling Ethyl Fluid and for mixing it with gasoline should be avoided. The most important means which can be taken towards this end is to send Fluid out of a plant only in such packages as can be used at properly designed mixing plants. Such plants, at present, employ only drums of 10 gallon and 55 gallon capacity. The distribution of small cans of Fluid, (i.e. one liter capacity), is an inevitably hazardous procedure and should be limited to the absolute minimum. Tin cans containing several liters of Ethyl Fluid are dangerous to transport and even more dangerous to handle in any present type of mixing equipment and should be completely avoided. A small number of cans of one liter or of smaller capacity is required at present for certain types of control procedures and for certain justified experimental

purposes. The use of such cans should be restricted to research, and to military, naval, and air-mail emergencies. Their distribution to irresponsible or uninstructed persons would be an act of carelessness and negligence. Indeed complete instructions as to procedure should accompany every can which is issued, and careful records should be kept of the destination of every such can. All sale and shipment of cans should be refused by the manufacturer except in such instances as the need for them can amply be demonstrated by the purchaser.

Not only is the use of numerous types of containers (especially small ones) dangerous beyond the limits of the manufacturing plant, but it is also unnecessarily hazardous within the blending plant. Safety in the blending and packaging operation depends fundamentally upon the simplicity and uniformity of daily procedures. Irregular practices and specialized operations are likely to create new and difficultly controlled hazards and should be kept at a minimum. Moreover the hazard of filling a small package is as great as that of filling a large one, therefore the packages should be as large and as few as possible with due regard to the limitation of hazard in transporation and in other types of handling beyond the limit of the manufacturing plant.

The drums employed for the shipment of Ethyl Fluid should be of exceedingly strong and durable construction, with I-beams on which they can be rolled, and with double bungs for the avoidance of leakage. Safety in the continued use of these drums will depend on the care taken in inspecting and repairing them when possible and replacing them when necessary. After every trip to a consignee each drum must be cleaned thoroughly, inspected critically for corrosion, injury, or leak and should be repainted. After being filled with Fluid

each drum should be tested for at least twenty-four hours by standing with the bung downward, and by carefully inspecting the seams for leaks. Such leaks will show up clearly on the freshly painted outer surface of the drum, if the Fluid is highly colored and if the drums are painted white or light grey. For this and other reasons which will appear later, the Fluid must be brightly colored for purposes of commercial handling.

Obviously, the opening, cleaning, and testing of returned drums are dangerous operations. They must be handled with highly specialized and thoroughly ventilated equipment if they are to be done thoroughly and safely. Actually it has been found to be wholly necessary to clean the drums thoroughly, not only for reasons of safety, but also for commercial reasons, since it is impossible to avoid the accumulation of scale and rust which will result in the presence of suspended matter in the Fluid, and will interfere with mixing operations by plugging valves and other small orifices. Such occurrences result in opportunities for serious lead exposure in mixing plants, and should be reduced to a minimum.

III. General Hygienic Measures and Facilities Required in the Manufacture of Lead Tetraethyl and in Blending Ethyl Fluid.

The potential hazards associated with the manufacture and blending of Ethyl Fluid are probably the most serious that can be found in any of the lead trades. However, they are capable of complete control if proper provisions are made to maintain an adequate degree of precision and caution in carrying out plant operations. It is exceedingly doubtful if this can be done unless the most rigid and critical medical supervision is established and maintained, but the experience of the past twelve years has proved that complete success can be assured by the means of measures of control recommended herein. It would be most unfortunate, in view of the demonstrated

adequacy of such methods, if cases of intoxication and fatalities were to occur in plants not so safe-guarded, since it would be quite obvious that such incidents were the result of carelessness or lack of regard for past experience.

The control measures consist of the following co-ordinated types of hygienic supervision, namely, (1) a continual clinical study of all workmen, (2) regular study of the magnitude of the lead exposure and lead absorption of representative groups of workmen through periodic determinations of the rate of lead excretion in the urine and feces, (3) regular periodic critical survey of plant activities and operations by the physician-in-charge, and (4) regular determination of the lead content of the air of all rooms and working spaces in the plant.

Clinical Work. Not only is it necessary to maintain a sharp search for clinical evidences of lead absorption, but it is also imperative that all types of illness among workmen be recognized and identified, if there is to be a proper degree of mutual confidence between the workmen and the medical staff. It is not enough to be on the lookout for subjective symptoms of incipient intoxication, or to watch for changes in the blood of workmen, or to see the cruder evidences of lead absorption. It is also necessary to recognize the occurrence and character of non-occupational disease and to see that it is adequately cared for or at least that it is brought to the attention of the workmen. These things cannot be accomplished by cursory and slip-shod examinations or by certain partially specific laboratory tests, but only by careful and regular study of each workman as a whole.

In these occupations each workman who is potentially exposed to lead tetraethyl should be examined at least once per month, while men whose work involves exposure only to dust and fume of inorganic lead

compounds should be examined at intervals of not more than three months. (It is advisable to examine the men more frequently unless and until it has been clearly established that the dangers of normal plant operations have been brought under adequate control.) At each examination each workman is questioned carefully in search of subjective symptoms and other evidences of incipient illness. The temperature, pulse, blood pressure, and weight should be noted and recorded, and the urine should be examined as to its reaction, and the presence or absence in it of sugar, albumin and microscopic abnormalities. Such other clinical study as is required to determine his physical status should be carried out, together with an examination of his blood, including, at least, the determination of the hemoglobin and a quantitative determination of the number of erythrocytes which show basophilic granulation, ("stippling"). The teeth and gums should be examined for sponginess or congestion and for the presence of a lead line, especially on the inner aspect of the gums opposite the molar teeth. The strength of the grip of each hand should also be determined and recorded. At least once a year each man must have a complete and detailed physical examination, including a general neurological examination.

An initial examination of a complete and thorough type should be employed as the basis for the selection of an essentially sound and healthy operating crew. The results of this examination should be carefully recorded in the case of all men accepted for employment and should be used as a basis for future comparisons. Workmen should be rejected:

(1) When they have had significant exposure to lead compounds in other occupations within the period of five years immediately preceding;

(2) When they have had an illness associated with a previous occupation which is indicative or strongly suggestive of lead intoxication;

(3) When they have a significant degree of organic disease of the circulatory system, especially symptoms and signs of arteriosclerosis;

(4) When they have organic disease of the nervous system, a history of epilepsy, or of functional disturbances associated with mental instability;

(5) When they have organic disease of the kidneys, liver or lungs;

(6) When they have other chronic diseases, such as oral and upper respiratory infections of a severe and potentially disabling type which, in the opinion of the examiner, are unlikely to respond to corrective measures;

(7) When they are excessively addicted to the use of alcohol, or when because of ignorance, stupidity, undue apprehensiveness, or other evidences of unreliability, they are unsuited to employment in a potentially hazardous occupation.

(8) When they are less than 21 years of age or more than 45 to 50 years of age.

Men should be removed from employment:

(a) When they develop symptoms suggestive of lead tetraethyl intoxication;

(b) When they develop physical signs and laboratory evidences of significant lead absorption.

(c) When they develop organic disease, which, in the mind of the examiner, involves undue risk to their safety and that of others;

(d) When they show a careless or irresponsible attitude toward the hazards of the occupation, or, alternately, when they show undue anxiety with respect to such hazards.

Excretory Analyses.

The study of the lead excretion of representative workers portrays a surprisingly accurate picture of the conditions of exposure to which they are subjected. The significance of such results cannot be discussed here but reference can be had to published information. Suffice it to say in reference to lead hazards which, like these, give rise to prompt and serious effects, that adequate hygienic control cannot certainly be maintained without such information. The methods employed in the collection of samples and in their analysis must have the utmost precision to be of value. In our experience this work cannot be done within the plant, but must be carried out elsewhere in order to avoid the contamination of samples from the plant environment.

The diagnostic value of the use of analytic methods on the blood and excreta, in suspected or doubtful cases of intoxication, cannot be over-emphasized. We believe that such facilities are absolutely essential to sound clinical work in this occupation, in view of the absolute necessity for the prompt interpretation of symptoms.

Plant Supervision.

The plant physician should make a critical inspection of the plant under operating conditions at intervals of approximately one month, at which time he should criticize all the procedures and recommend such changes as are advisable for the maintenance of safety.

Air Analyses.

Equipment should be installed and operated regularly to test the air of all working spaces for its lead content. Long pipe lines and rubber hose lines must be avoided in collecting air samples for analysis, in order to avoid condensation and absorption of lead tetraethyl in the carrying lines. A high degree of accuracy is necessary both in the collection of samples and in the analytic procedures.

All the data referred to above should be reported to the physician-in-charge and should be used by him to keep himself and the management fully informed as to the hygienic status of the plant as a whole.

Clothing, Protective Equipment, and Washroom Facilities.

Excellent facilities must be made available for the protection and cleanliness of the workmen. Each workman must be provided with complete clothing, so that he may not, under any circumstances, make use of his regular clothing in the plant. There must be a system of double lockers, and comfortable and adequate washrooms, shower baths and toilets. At the beginning of the day's work the workmen must change into work-clothing. At lunch-time they must wash carefully and eat their lunch in a clean lunch room. At the end of the day they must remove all their clothing, bathe and change into their own clothing. The proper arrangement of these facilities will not only add to the willingness of workmen to comply with the regulations, but also will provide for such supervision as will not permit carelessness on the part of the workmen.

Impervious gloves, dust masks where required, and air-line masks as needed, must be supplied and maintained in satisfactory condition by the management of the plant.

IV. Hygienic Aspects of the Transportation of Ethyl Fluid.

The spillage of Ethyl Fluid in transit may cause serious difficulties in that dangerous exposure may involve carriers as well as other persons who may have no knowledge of the dangers and no means of protecting themselves. Moreover, other commodities may be so contaminated as to cause the dissemination of serious danger into remote regions. The utmost care should be exercised to confine the hazards to points at which they can be controlled.

Drums of Ethyl Fluid shipped by rail should be secured by suitable means so as not to move about in transit. They should not be mixed with other cargo but should be sent direct from manufacturer to mixing plant and should be handled at both ends only by trained and experienced persons. Drums of Fluid transported by water should be loaded on deck under the supervision of fully informed and experienced persons, and should be secured firmly in place so as not to be damaged and so as not to be a source of danger in transit. Any Fluid which may leak or spill on the deck of a ship or barge should be washed overboard promptly and any leaking or broken drums should be disposed of by being cast overboard if possible or necessary, or by being so placed that further leakage will not occur. Every practicable safeguard should be thrown around this phase of the industry and to the extent that this commodity requires unusual care in transport, it should be incumbent upon the manufacturer and shipper to provide conditions compatible with reasonable safety.

Cans for the distribution of small quantities of Ethyl Fluid should be strong and of a well designed type for pouring without dripping. These should be encased in a second, hermetically sealed metal can, so that no leakage can occur in transit, and complete instructions for handling a can with safety and for disposing of it when

it is empty should be enclosed within each outer can. Persons who may use them inadvertently or such persons as aeroplane pilots cannot be expected to appreciate the risks associated with improper handling of the material and should be both warned and instructed. It should be said, in this connection, that there is no need for aviators, either civil or military, to prepare their own gasoline by the addition to it of Ethyl Fluid. It has been found to be feasible to obtain gasoline of suitable quality, at practically any point designated, by specifying what is needed and giving the regular manufacturers of such gasoline an opportunity to supply it. Moreover, the results of such methods of obtaining gasoline will certainly be found to be gratifying, in that a more uniformly satisfactory fuel will thereby be obtained. The indiscriminate and unnecessary use of cans of Ethyl Fluid should be discouraged therefore by every means which is at the command of the hygienic authorities.

V. Precautionary Measures in Mixing Ethyl Fluid with Gasoline at Refineries and Bulk Terminals.

Little need be said at this time concerning the proper way of handling this procedure. The general principles of methods employed up to the present are known by most of the gasoline refiners and distributors. The regulations which have been in use for the operation of mixing plants have received extensive circulation in the industry and among hygienic authorities in the states. These provide a complete and adequate basis for the formulation of official codes, except that no reference is made in them to the frequency or the technique of the medical supervision. It is believed that safety in this field can be accomplished only by strict adherence to the use of properly designed equipment and adequately regulated and supervised technique. Detailed

information will be supplied at any time it may be desired.

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