Ethyl Fluid and
Ethyl Gasoline- Photos, etc.

Hazards in the Handling of Ethyl Fluid and Leaded Gasoline

by

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Certain Properties of Tetraethyl Lead

The hazards associated with the manufacture and handling of Ethyl Fluid are due almost wholly to the physical, chemical and toxicologic properties of its principal constituent, tetraethyl lead. This compound of lead is a water-white oily liquid with a specific gravity of 1.67, almost twice that of water. It boils at a temperature of about 200°C and has an appreciable vapor pressure at ordinary temperatures, so that air saturated with its vapor at about 25°C contains approximately 5 milligrams of lead per liter. The oil has an almost unique ability to creep through seams, valves and pipe fittings, it penetrates rubber gaskets with considerable rapidity, and is in many ways a difficult material to handle without leakage. Moreover when spilled it is not easily cleaned up, since it soaks into wood, asphalt and earth with which it comes in contact. In the presence of light or air it tends to decompose slowly, yielding triethyl lead salts and other crystalline organic lead compounds.

For this reason storage tanks, drums, small containers and pipe lines used to convey Ethyl Fluid may have variable amounts of crystalline deposits within them, which offer considerable resistance to cleaning procedures. Tetraethyl lead ignites at high temperatures, and while Ethyl Fluid is considerably less inflammable because of its content of organic halogen carriers, it behaves similarly at somewhat higher temperatures. On ignition the organic lead compound is decomposed and distributed into the air in a very finely divided state, (essentially smoke).

Tetraethyl lead is absorbed through normal unbroken human skin, which it penetrates without producing painful sensation or appreciable local injury. Its decomposition products do not pass through the skin to any significant degree, but they produce a stinging sensation and redness when the skin is moist with perspiration.

Lacrimation occurs when finely divided particles come into contact with the eyes. The vapors of tetraethyl lead, somewhat pleasantly aromatic in odor in their pure form, cause little irritation to the respiratory membranes, but are readily absorbed. A musty, garlic-like odor is associated with the products of early decomposition, and these compounds are irritating when inhaled, causing a burning sensation and vigorous sneezing. The odors of both pure tetraethyl lead and its decomposition products are characteristic and are capable of recognition and identification at extremely low concentrations.

When absorbed into the body tetraethyl lead is at first distributed after the manner of an oil-soluble material. It is subsequently broken down and redistributed according to the characteristic pattern of inorganic lead compounds. It is excreted somewhat more rapidly than inorganic lead compounds, but apparently will accumulate in the body as do the latter, when the rate of absorption is sufficiently high.

It is of the utmost importance that a material of this type be handled with great care. Not only must workmen avoid inhalation of vapors and contact of the skin with Ethyl Fluid, while handling the product, but they must also exercise considerable caution against the inadvertent handling of containers and pipe lines which have been contaminated with it. The potential dangers of exposure to the liquid and its vapors are greatest, for obvious reasons, in the manufacture of tetraethyl lead and in the preparation of commercial anti-knock Fluids. However these dangers can be controlled effectively through the consistent application of precautionary measures, and with comparative ease, because of their sharp localization in a few plants which can be closely supervised and carefully maintained. The hazards associated with the transportation of the Fluid, and its blending with gasoline, on the other hand, are diffuse, having been introduced into all parts of the country, and actually, at present , into all parts of the world. There are about three hundred refineries and terminal points in the United States alone to which Ethyl Fluid (or Q Fluid) is shipped for mixing into gasoline.

General Considerations of Safety in Blending Ethyl Fluid with Gasoline.

At the beginning of the large-scale commercial distribution of Ethyl Fluid it was obviously imperative that mixing equipment of simple and essentially uniform design be employed, and that simple but precise methods of procedure be developed and so established in practice as to provide complete freedom from hazardous lead exposure on the part of the mixing personnel. Accordingly the distributor of Ethyl Fluid undertook through contractual means to prescribe and to control the character of mixing equipment and the detailed manner of its use. Some friction was encountered in the initiation of this program. In some instances refinery managers and engineers were strong in the belief that they could devise more convenient and more satisfactory equipment and methods than could the relatively inexperienced (with reference to the petroleum industry) technical staff of the distributor of Ethyl Fluid. Indeed after twelve years there is an occasional vigorous complaint against the operative procedures required of gasoline distributors by the purveyor of Ethyl Fluid. To the extent that such complaints are an expression of resentment against what appear to be arbitrary measures of control, they deserve a sympathetic hearing. Mention is made of them here, however, only because in general they denote a fundamental though understandable lack of appreciation of the nature of the hygienic problem presented by the use of an inherently dangerous material such as Ethyl Fluid at widely scattered petroleum refineries. It would be hard to imagine all the types of equipment, and the variety of techniques that would have been used if the manner of mixing had been left to the discretion of gasoline manufacturers. In view of the varied experience, the ingenuity, and the independence of engineers in the petroleum industry, there can be little doubt that many methods would have been tried and that a number of them would have been found to be wholly satisfactory. Some, doubtless, would have given rise to serious difficulties. Unfortunately the adequacy of equipment and methods in relation to safety could not be determined except by a period of use, during which a proper regard for the lives and health of workmen demanded clinical supervision and experimental study to determine the facts with regard to the lead exposure associated with mixing procedures. Since there was a limit beyond which such supervision and investigation could not be extended effectively, the only feasible program was believed to consist in the restriction of the problem by fixing the responsibility for the design of mixing equipment, the methods of its use, and the investigation of its potential hazards in the hands of one organization. A further contraction of the potentially diffuse danger was effected by carrying out as many as possible of the hazardous operations at the Ethyl Fluid manufacturing plant, limiting refinery mixing operations to the simplest possible procedures, and making use of equipment designed to operate with little or no need for repair and having no moving parts in contact with concentrated Fluid. Thus two basic principles were involved in the formulation and application of a safe program for refinery mixing operations. (1) Operative procedure and equipment were to be adopted or modified on the basis of the results of a maintained investigation of the immediate and remote hazards attendant upon their use. (2) Refinery mixing plants were to be freed of all hazards which could be centralized at an Ethyl Fluid manufacturing plant, in order to eliminate types of exposure that required the exercise of uncommon caution and skill, as well as special ventilating equipment. The importance of the application of these principles to the solution of this hygienic problem cannot be over-emphasized. They are stressed here at the risk of being repetitious, because in our opinion they are the essential elements in a policy that must be maintained if safety is to continue in association with mixing operations.

It is apparent that the number of mixing plants should be kept at the lowest figure compatible with sound practice in gasoline distribution. The producer and distributor of Ethyl Fluid cannot, for obvious reasons, exert more than a persuasive influence upon gasoline distributors in this regard. Control here must be exerted by the gasoline distributor, who should recognize the advisability of limiting the hazard by avoiding the installation of unnecessary mixing plants, especially those of small capacity which are operated irregularly and infrequently, and those situated in relatively unimportant places, in the commercial sense. The operators of such plants are almost inevitably led to handle their work with some indifference and are prone to fall into somewhat careless and irregular practices.

The original equipment * for mixing Ethyl Fluid with gasoline consisted of the use of an eductor activated by a stream of gasoline, the Ethyl Fluid being drawn into the gasoline stream where it was promptly diluted. The drum of Fluid served as the unit of measurement whereby definite quantities of Fluid were introduced into known volumes of gasoline. This was a highly satisfactory and simple type of equipment, and it remains so under suitable circumstances. With increasing consumption of Ethyl Fluid, however, and with the consequent necessity for handling large volumes of Fluid and gasoline, a new type of equipment was developed, consisting essentially of a storage tank for Ethyl Fluid, mounted on scales and housed in a building,

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* There was a brief period of essentially experimental distribution in which a small metering device was employed on pumps at service stations. There was another short period in which various types of pumping devices were employed at bulk gasoline terminals and at a number of refineries. The eductor type of equipment, adopted in 1926, displaced all other types.

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and connected to a closed system of pipes, filling and emptying being accomplished by an eductor. Ideally, Fluid storage tanks are filled from tank-cars of Fluid of corresponding size, although in some instances, where circumstances require, they are filled with Fluid from drums. They are partially evacuated (to a desired weight) as required, by operating the eductor, mixing operations being carried out without exposure to the Fluid or its vapors. This type of equipment aided in the elimination of certain hygienic problems associated with increasing volume of distribution, and it introduced a new difficulty. By this time it had become apparent that provision should be made for more uniform and in some instances for more direct transportation of Fluid. In fact, the results of a study of the hazards of transportation provided one of the major reasons for tank-car shipments of Fluid. The chief disadvantage arising from the use of storage tanks for Ethyl Fluid at refineries consisted in the necessity for the periodic removal of decomposition products of the Fluid which sometimes were deposited in considerable quantity and eventually caused interference with the mixing procedures. The hazard of cleaning these Fluid storage tanks, recognized as too great to be handled adequately by the mixing personnel at refineries, was overcome by the development of special mobile cleaning equipment operated by a crew from the plant at which the Fluid was manufactured. This procedure was based on the policy of maintaining a centralized control of significant hazards.

Specific Hazards and Safety Measures in Mixing Plants

In the case of mixing plants supplied with Ethyl Fluid in drums, the principal hazards consist of the possibility of physical have been set up, and instructions have been provided in booklet form and by means of placards posted at mixing plants. These are matters of record and need not be detailed here.

The problem of safety in mixing plants that employ Fluid storage tanks and tank-car deliveries of Fluid, is somewhat different in detail but not in principle. Here again plant construction is based on specifications and operative procedure is subject to precise instructions.

Mixing plants in general are subjected quarterly to a critical inspection made by safety engineers representing the distributor of Ethyl Fluid, and to at least an annual inspection by a member of the corresponding medical staff, who also examines each member of the mixing personnel. Complete records are kept of the results of the plant inspections, and of the clinical data. From time to ti o injury from the handling of the heavy, bulky drums of Fluid, the opportunity for skin contact with Fluid and exposure to its vapors, from opening and closing the drums and from spillage and leakage. In addition to these regular or normal operative hazards, there are infrequent or accidental hazards associated with the repair of equipment and the dismantling of obsolete or abandoned mixing plants, as well as the ever-present danger of fire.

Safety from physical injury and from fire is primarily a matter of the location and design of mixing plant and equipment, whereas freedom from lead exposure can be achieved only by the combination of properly designed equipment and precise operative techniq[ue]. In any case, plants must be built on specifications which have withst[ood] the test of practical experience, and they must be operated on the bas[is] of instructions which have proven their adequacy. Such specification[s] studies are made of the occupational lead exposure of selected representatives of the mixing personnel in various parts of the country, as indicated by their urinary and alimentary lead excretion. The clinical and laboratory studies have demonstrated that the specified types of mixing equipment are wholly adequate to prevent measurable occupational lead exposure when operated in accordance with the prescribed technique.

The supply of Ethyl Fluid available in drums or in storage tanks at numerous gasoline refineries has been and continues to be a source of temptation to persons who wish to obtain small quantities of Ethyl Fluid for their own use. Efforts have been made repeatedly, and sometimes with success, to put pressure on some employee of a gasoline distributor to obtain and release Fluid by sale or gift. There have been occasional thefts of Fluid sometimes for resale, and sometimes for personal use. There have been occasions also where a small or large quantity of gasoline at some point remote from a mixing plant was in need of Ethyl Fluid to bring it up to certain requirements as to quality. At such times the urge to make use of irregular mixing practices has been great, on the part of gasoline distributors, and some gasoline manufacturers have been disposed to feel that since both gasoline and Fluid are their property, they should be entitled to deal with them as they choose. All such situations are difficult to handle. Theft and the misuse of Fluid provide dangers which cannot be entirely prevented, and except for the possible consequences to wholly innocent persons, any considerable anxiety over this problem would be unjustified, because of the small quantities of Fluid involved and the infrequency of such occurrences. The use of Fluid for proper purposes but by improper means, on the other hand, is a much more serious matter, since it usually means an enforced acceptance by refinery employees of risks forbidden in standard practice, and since uncontrollable hazards of a remote type are likely to be incurred. Further reference to these remote hazards will be made later. The cardinal principle which should dominate all mixing practice in the interest of a reasonable safety, is that Ethyl Fluid should be mixed with gasoline only by means of equipment which has been designed for that purpose, and by methods which have been tested by investigation and practical experience.

<u>The Hazards Associated with the Transportation of Ethyl Fluid</u>

One could imagine certain rather gruesome possibilities as the outcome of accidents in the rail and water transportation of Ethyl Fluid. Only a few of the possible difficulties have been realized or suggested by actual occurrences over the period of years involved. The most significant of them was the contamination of a mixed cargo of materials, in part foodstuff, by damage to a drum of Fluid improperly transshipped by local freight. Another potentially dangerous incident was the perforation of a drum of Fluid, which escaped from its lashings on shipboard. Occasional drums have sprung leaks, by reason of rough treatment in transit, from improper handling at destination, or in rare instances, as the result of previously unrecognized minor defects in a drum. The warning to be drawn from these incidents is clear. When shipped by rail Ethyl Fluid drums should be secured against movement in a car, and should not be in mixed cargoes, but should go direct to destination, where they can be received and handled by informed persons. Such precautions will prevent danger to employees of the carrier, and will guard against the contamination of other commodities. When transported by water, drums should be lashed securely on the deck of a ship where any leaking Fluid will be noted and readily hosed away, and where vapors cannot be confined.

The use of tank-cars for rail shipment of Fluid has largely solved the difficulties of transportation, and considering the great distances that must be traversed in the United States, such means of transportation is greatly to be recommended as a matter of safety. However to the extent that drum shipments continue, by rail, or more particularly, by water, there is always a potential hazard, which must be combatted by detailed attention, on the part of consignor and consignee, to proper methods of loading and unloading freight cars and ships. The study of transportation problems is maintained as part of the safety program of the distributor of Ethyl Fluid, and from time to time recommendations are made for the correction of potentially hazardous situations.

Carloads of drums have been involved in wrecks, and in one instance almost an entire carload was destroyed in the fire that followed such a wreck. Tank-cars of Fluid also have been involved in minor accidents, but without any serious consequences. Shipwrecks and railroad wrecks, obviously,cannot be anticipated and guarded against by a consignor, but the situations which result from such accidents to cargoes of Ethyl Fluid can be handled without undue danger of lead intoxication if prompt action is taken by properly informed persons. For this reason the attention of carriers and others is called by suitable placards, to the fact that representatives of the distributor of Ethyl Fluid should be notified of the occurrence of an accident, by the most expeditious means.

Drums of Fluid are sometimes transported for comparatively short distances by automobile trucks. The precautions required for trucking Fluid are similar to those carried out in rail shipments, but in addition attention must be paid to the weight-bearing capabilities of the truck, to the instruction of the driver as to the dangers to himself and to others which must be avoided, and to the intelligence and reliability of the driver, with respect both to highway traffic and the handling of the Fluid. Here again drums of Ethyl Fluid should not be mixed with other commodities in transit. Tank-trucks are also employed by the distributor of Ethyl Fluid on short hauls. The problem here differs from that of rail tank-cars only in so far as the hazards of highway traffic differ from railroad traffic. The greater dangers of collision on a highway are offset in some degree by the actual presence of two informed persons (the driver and an assistant) on each cargo.

<u>Hazards Associated with Gasoline After its Blending with Ethyl Fluid</u>

As has been pointed out previously, the properties of tetra-

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gasoline itself. It is scarcely necessary to mention the inflamma-bility and the explosive properties of gasoline. All manufacturers and distributors of gasoline know that gasoline vapors will produce asphyxiation by exclusion of air in enclosed places, and that in high concentration, even in the presence of adequate air supply they will cause rapid unconsciousness and death. It is apparently not so well appre-ciated that concentrations of gasoline vapor in air in excess of 1 to 1.5 percent by volume cannot be endured for more than a few minutes, and that concentrations in excess of 0.5% by volume are hazardous for more than short periods of inhalation. Moreover, although it is well known that burns of the skin are produced by gasoline, persistent and recurrent dermatitis is not recognized by more than a few gasoline distributors to be an occasional consequence of repeated and regular contact of the skin with gasoline. During the past fifteen years since the introduction of leaded gasoline into commercial use, a number of cases, entirely typical of the effects of the inhalation of toxic concentrations of gasoline, as well as others characteristic of the results of skin contact have been brought to my attention by representatives of gasoline distributors who were not aware that gasoline could produce such effects, and who thought these might be cases of lead poisoning among gasoline handlers. I have also seen a few cases of illness among persons who have swallowed gasoline in siphoning from a fuel tank or otherwise. Here the symptoms were those of the intense gastro-intestinal irritation characteristic of gasoline effects, associated with some degree of general intoxication where appreciable gasoline absorption had occurred. In no instance was there evidence of lead intoxication, nor would any such result be expected if one took the trouble to calculate the quantities of lead ingested with the gasoline. Indeed, we may dismiss the entire matter of any peculiarly toxic properties of commercial leaded gasoline, as differentiated from corresponding non-leaded gasoline, by pointing out that neither my associates nor myself have seen or have been able to find evidence of the occurrence of a single case of lead poisoning or of lead absorption from skin contact with or inhalation of leaded gasoline among the thousands of persons at refinery loading racks and filling stations, or among tank-wagon drivers and other handlers of large and small quantities of gasoline. Our field studies and the experimental observations which provide an explanation of the non-injurious effects of commercial concentrations of Ethyl Fluid in gasoline have been discussed elsewhere and need not be mentioned here. Suffice it to say, that at present there is no reason to believe that there are any greater dangers from contact with leaded gasoline in its liquid or vaporized state, than there are from similar contact with the base gasoline alone.

<u>Lead Hazards in Cleaning and Repairing Gasoline Storage Tanks</u>

Despite what has been said above about the innocuous character of contact with leaded gasoline, from the standpoint of lead absorption, significant opportunities for lead exposure exist in connection with the cleaning and repairing of tanks used in blending Ethyl Fluid with gasoline, and to a lesser extent, of tanks used for the prolonged storage of leaded gasoline. A number of factors are active in the production of these opportunities and since a comprehensive study is being made to determine the relative importance of individual factors, it would be premature at this time to attempt the complete elucidation of the problem. However, certain facts which are quite clear may be pointed out as the basis for measures of safety which have been put into operation to an increasingly effective degree over a period of years.

If Ethyl Fluid is introduced into gasoline by merely pouring or piping the concentrated Fluid into a receptacle which contains gasoline overlying a layer of water, some portion of the heavy Fluid may settle rapidly through the lighter gasoline and through the water layer as well, forming a layer of the Fluid at the bottom of the receptacle. Under suitable circumstances, moreover, Fluid which is diluted with gasoline, but so slightly as to have a grossly higher specific gravity than that of water, may behave as above and sink to the bottom of a blending tank. The water layer separates the Fluid or the insufficiently diluted Fluid, from the gasoline into which it was to be distributed, so that the Fluid remains at the bottom indefinitely. To the extent that this situation has occurred, as the result of various types of faulty mixing operations, it is apparent that blending tanks will contain quantities of Ethyl Fluid in the sludge at the bottom of the tank, to be encountered when the tank is cleaned, regardless of the length of time intervening. It is this serious hazard, which arises from improper and unsatisfactory mixing operations, to which reference was made in a previous paragraph. It is obvious that concentrated Fluid should not be poured into any gasoline receptacle which is not provided with adequate means for complete admixture of its contents. Ideally the Fluid should be introduced into a gasoline stream entering the receptacle, at such a rate as to insure its high dilution with gasoline. Obviously, the closer the entering dilution is to the desired dilution, the more certainly satisfactory is the mixing operation, from the standpoint of the avoidance of stratification of the Fluid, and the shorter will be the time required for further mixing by recirculation.

Another source of potential lead exposure in tanks used for blending and storing leaded gasoline arises from the slow decomposition of tetraethyl lead in the mixed gasoline to form crystalline lead compounds which are deposited in the scale on the sides of the tank, and which gradually settle out into the sludge at the bottom of the tank. The rate of this decomposition is quite slow, and the quantities of crystalline lead compounds formed are minute indeed as compared with the quantities of tetraethyl lead which remain unchanged in the gasoline. Nevertheless over a period of years an appreciable amount of scale (mainly iron rust) containing triethyl lead salts, may form on the sides and at the bottom of the tank. If the tank be emptied and if the scale and sludge be permitted to dry out, any mechanical operation which involves the walls or floor of the tank, or which dislodges either scale or sludge, will suspend some quantity of finely divided, lead-containing particles in the atmosphere of the tank where it may be breathed by unprotected workmen. In general, the quantities of lead in the scale on the s[illegible] of a tank are quite small, and there is reason to believe t[illegible] only under unusual circumstances would a dangerous degree of l[illegible] exposure originate from this factor alone, but one must take into account that the essentially enclosed volume of atmosphere in a tank may become progressively more highly concentrated with respect to dusts arising from its walls in the period of hours during which workmen are cleaning or repairing the side walls.

Therefore, from the viewpoint of the investigator, the potential lead exposure associated with prolonged scraping, hammering, riveting and welding operations on the dry walls of storage tanks must be regarded as potentially significant until it has been shown to be negligible. The lead exposure from this source can be prevented with comparative ease by keeping the side walls of a tank wet while cleaning and making repairs. * A light oil applied over the entire surface has also been found to be satisfactory in preventing dusts. In one instance in which observations were made on the lead exposure of a group of workmen over the entire period required for dismantling a large storage tank, after the use of such an oil on the side walls, no evidence of lead absorption could be detected.

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* This statement must not be taken to mean that the dangers of lead exposure in a tank are thereby avoided, for the sludge at the bottom of the tank is likely to be a more important source of such exposure.

vapors. Accordingly, in our opinion, instructions for the avoidance of lead exposure in cleaning leaded-gasoline storage tanks at

types of air-line respirators as standard safety equipment for such work.

We have made no reference in the foregoing discussion to the relatively small gasoline storage tanks used by jobbers and others at local marketing points, to service-station gasoline tanks, or to tank-cars and tank-trucks. Standard safety practices in deali

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* Observations on a large number of samples of sludge have shown tha relatively large quantities of litharge may be found occasionally in the deposits in the bottom of gasoline storage tanks.

The sludge at the bottom of tanks may be found to be little if any more dangerous with respect to the lead content - than the scale on the walls of a tank, except where Ethyl Fluid has found its way into it through some such means as those indicated previously. In any case precautions should be taken, not only agai the lead compounds which may be present, but also against the volat! compounds (petroleum fractions) which continue to be given off as vapors from such sludge. Quite a few experienced refinery managers believe that uncleaned gasoline storage tanks should never be entere for any reason except by persons who are equipped with air-line respirators, and xxx are under the continued supervision of observers on the outside. If refinery experience has justified such precautio and it would appear to have done so amply, it seems only the better part of wisdom to adopt means for the avoidance of respiratory lead exposure which are in line with such protection against gasoline with these must take care of the hazards associated with respiratory and cutaneous exposure to gasoline, but there is no present reason based on experience or experimental observations, for believing in the existence of danger from lead absorption in connection with the normal handling of such equipment. In view of investigations now under way, to which previous reference has been made, it would be injudicious to go into a detailed discussion of the different factors which combine to minimize the potential lead exposure in connection with these tanks, or to absolve them from any question of lead hazard by a categoric statement.

A practical program for the elimination of dangerous practices in connection with the cleaning and repairing of leaded gasoline storage tanks has been promulgated by the distributor of Ethyl Fluid, through the issuance of instructions for the avoidance of lead exposure in tank-cleaning operations. Provision has been made for the more effective application of these instructions, and, at the same time, for the accumulation of more precise knowledge of the opportunities for hazard in connection with current practice, through the maintenance of a comprehensive supervision of tank-cleaning and tank-repairing activities at refineries and bulk terminals, by safety engineers representing the distributor of Ethyl Fluid. Real safety here as well as in other fields of accident prevention in this and in other industries, is believed to be best achieved not by setting up increasingly stringent regulations following the occurrence of accidents, but by continued study of operating methods with respect to the type and magnitude of the hazards attendant upon their use.