ply including fire protection water, location and adequacy of sewers including the eventual disposal of sewage, type of ground, whether the area is subject to floods, and even the direction of wind. All are part of a properly designed installation.

Finally, in working up a safety program for solvent-extraction plants, it must be held in mind that ordinary and usual safety considerations must not be minimized because of the emphasis on special safety considerations. A man can just as easily catch his heel on a stairway and break his leg in a solvent plant as he can in an ordinary building.

An important improvement in safe operation in the last 15 to 20 years, during the time that I have been observing this operation, has been the simplification of extraction plants themselves. Improvement in engineering and operating efficiency makes for a safer plant in itself. Combined with this has been a corresponding improvement in the efficiency of safety devices and in safety design.

Safety in Solvent Extraction from the Viewpoint of Insurance and Practical Operation

ODELL J. JONES, HORACE R. BELEW, and ORVILLE L. WILLIAMS,
Western Cottonoil Company, Abilene, Texas

WHEN THE A.O.C.S. Technical Safety Committee met in Houston in the spring of 1956, one of the principal topics of discussion was the proposed schedule for rating solvent-extraction plants in Texas. With this in mind, two questions present themselves: why is a rating schedule of this type necessary, and what functions are accomplished by such a schedule? Please bear in mind that we are not opposed to having a rating schedule of this nature. Certainly a schedule is necessary from an insurance standpoint, and it is helpful in many other ways, such as serving as a guide for new construction and as a spot check on various phases of safety in every-day plant operations. If solvent extraction itself is a practical operation, then any schedule that is adopted necessarily must be made to produce an equitable rate, and it also must be practical from an operator's standpoint. We have cooperated wholeheartedly with state agencies and interested insurance companies in trying to make this schedule practical as well as realistic, something we feel that the industry can live with. Thus far the undertaking has proved to be a sizeable task. We are confident that with enough effort and with men and committees, such as the one we have here, working at it, we shall come up with a schedule that will prove to be beneficial to all concerned.

The State of Texas has under consideration a proposed schedule for rating continuous process solvent-extraction plants, using flammable liquids having a closed cup flash point below 110°F. There are nine of these plants now operating in Texas; eight extract oil from cottonseed and one from rice bran. There were formerly two "rice" plants; however one has ceased operation. Four of the cottonseed plants and the one handling rice are insured in "admitted" companies, and it is understood that the others are insured by "non-admitted" organizations.

At the present time there is no schedule for rating these plants in Texas and, so far as can be determined, there is no schedule in any of the rating jurisdictions. The process is relatively new here, and it is believed all who have assisted in setting up the proposed schedule will admit that it has been erected on a judgment basis. It is recognized that there is no other way; however it is believed the end-safety result should be weighed against the end result in the application of an existing schedule which has some common hazards or processes. Again, there is no credible experience, so far as is known, to which this proposed schedule can be tied. It is believed that knowledge gained as operators should enable us to suggest improvements as well as to point out the obvious inequities of the proposed schedule. This proposed schedule, like that for petroleum properties, is unusual in that it provides on page 16 that "this rating schedule is complete in itself and rates produced hereunder are not affected by rating rules contained elsewhere in G.B.S." Again it is unusual and follows the petroleum properties schedule in making inherent explosion coverage inseparable from the fire coverage, providing a combined fire and inherent explosion rate. This proposed schedule which is set up for solvent plants, using flammable liquids having a closed cup flash point below 110°F., stresses the principal fire and explosion hazard as being from the flammable solvent used in the process.

SIMILARITIES to the Texas Petroleum Properties Schedules and the fact that flammable liquids are indicated as the chief hazard suggest that the gasoline plant schedule (Texas General Basis Schedules for Petroleum Properties, pp. 22–24) is the nearest one we can find for comparison with the solvent plant. Gasoline plants deal entirely with light liquids and gases, at high pressure (600–3,000 lbs. and in rare cases up to 5,000 lbs.) and at high temperatures (700–900°) whereas the solvent plants under consideration deal with solids and liquids at low pressure (atmospheric or vacuum) and at low temperatures (under 230°F.), which are below the ignition point of the solvent. They may also carry a maximum absolute steam pressure of 140 lbs. on some of the steam-jacketed vessels. This is for heating purposes only.

For comparative purposes, minimum rates will be used since they represent those plants built according to standards with all superior feature credits applied. Any deviation from standard either in construction or occupancy will be represented in the deficiency charges. Therefore for a true comparison only minimum rates should be used.

It appears that the gasoline plants, dealing in higher pressures and temperatures and in lighter

fractions of petroleum, would be a great hazard; however the minimum annual fire and inherent explosion rate for gasoline plants, before credit for fire divisions, is .20 while the minimum annual rate under the proposed schedule for rating solvent plants is approximately .38. This .38 minimum rate includes a very high credit for automatic combination deluge and water spray protection whereas the Petroleum Schedule produces a much lower rate without an expensive protection feature such as this. It is thought that this inequity in mimimum rates should be removed by making the proposed solvent schedule produce a minimum annual fire and inherent rate of explosion nearer .20.

Some plants to be rated under the proposed solvent schedule provide insurance to cover unfired pressure vessels from damage caused by internal pressure or vacuum. The companies writing this insurance provide an inspection service which is calculated to prevent an accident. Damage to these vessels caused by internal pressure is also covered by the inherent explosion clause in this proposed schedule. Consequently there is an overlapping coverage and insurance for pressure vessels since operators who carry pressure vessel insurance believe that it must be continued for two reasons. First, it provides a coverage which is not included in the fire and inherent explosion schedule. Then the inspection service is invaluable in the prevention of accidents. It would be inequitable to pay the same rate on a plant where the service and insurance are furnished as in a plant where it is not provided; therefore it is thought that the proposed solvent schedule should provide a credit of 10% from the final rate where pressure vessel insurance is carried on all metal unfired pressure (other than static pressure) vessels permanently located on the premises of the assured and forming a part of the solvent plant.

By the same token it is desirable to remove the inequity in the windstorm and extended coverage rates produced under the proposed schedule. The schedule for rating gasoline plants (Texas General Basis Schedules for Petroleum Properties) recognizes that "inasmuch as the hazard of inherent explosion is contemplated in the fire rate produced by the application of this Schedule, the rates for Extended Coverage Endorsement shall be based upon a minimum explosion classification." The proposed solvent schedule also contemplates the inherent explosion hazard "in the fire rate" and therefore should follow the procedure of the Petroleum Schedule under which the (inland) annual 90% co-insurance extended coverage rate for an ICM gasoline plant is .054. Under the solvent schedule a building of the same construction will rate .11 if of open construction, or .14 if enclosed.

The Petroleum Schedule also provides a lower windstorm rate for ICM building, and it is thought that the same treatment should be used in the case of solvent-extraction plants.

A reclassification of the rate for explosion is desirable, excluding inherent explosion from Grade of Occupancy 2 to Grade of Occupancy 1. Explosion rates are composed of two factors. One measures the hazard inherent in the occupancy, and the other measures all other explosion hazards. The inherent factor is reflected in four separate classifications referred to as Grade of Occupancy. To illustrate, a dwelling is rated under (the lowest) Grade of Occupancy 1 while a grain elevator with its dust hazard is rated under Grade of Occupancy 3. The other factor is a constant. A risk within 10 ft. of explosives takes the same Grade of Occupancy as if it were 10 miles away. A dwelling is always classified Grade 1, and a grain elevator is always classified Grade 3, no matter where it is situated. Therefore, following the theory for rating explosion risks and recognizing the charge for inherent explosion as being included in the rate, Item 8, p. 18, should provide that Explosion (excluding inherent explosion) should rate according to general rules, Grade of Occupancy 1.

To facilitate rating of unallied risks it is suggested that the exposure tables of the Texas General Basis Schedules refer to the Solvent Schedule for the specific exposure charges from the solvent plant or that these charges be incorporated in the Exposure Table section of the Texas General Basis Schedules.

The first sentence of this proposal sets the tone for this, in some cases, impractical schedule by requiring employment of "only competent personnel experienced in the fire and explosion hazards of flammable liquids." The definition of "competent" and "experienced" becomes important. There are degrees of competence and degrees of experience. Is a man "experienced" who has worked in a filling station pumping hazardous liquid into automobiles? Is a man "experienced" who has worked in a refinery or has driven a butane or gasoline delivery truck? Some would say that such experience is as likely to create a hazard as to prevent one and most certainly adds nothing to the safety of a solvent-extraction plant. There is no reservoir of experienced solvent-plant personnel on which to draw, and there is not likely to be such a reserve. The reasonable thing is to use employees who have proven that they are conscientious, careful, reasonably intelligent and are loyal enough to stay with you. They are much safer than "experienced" strangers who may be careless one day and gone tomorrow. This is an example of use of terms in applying well-intended but mistaken guidance to solvent plants in an effort to obtain accident-proof operating conditions. As a further example, it should be mentioned that the proposed schedule says "adequately curbed and drained;" many operators would not want to be ruled by this designation or rather by someone's interpretation of it. Likewise one might ask, "what is the meaning of phrases such as 'properly detached' and 'properly located'?" The proposed schedule states that all equipment and buildings shall be "effectively grounded." A great deal of work has been done on this problem by insurance companies, experimental laboratories, business firms, and the U. S. Department of Agriculture. In some cases all of these have failed. According to a dictionary, "effectively grounded" means "grounded with the desired effect being obtained." Such is not always possible. It is agreed that equipment and buildings should be grounded, but one cannot be assured that the grounding will be "effectively grounded." Therefore the word "effectively" should be deleted.

In an enclosed building a change of air is required every five minutes; in a cold climate this would probably be prohibitive because of the cost of warming the air enough to live in it. Perhaps a more practical system would be simply an exhaust fan with

a manual control to be on at the discretion of the operator. He could be warned by an automatic flammable vapor detector or by his own knowledge of conditions in the plant.

The "non-silencing alarm" and its switch which gives "visual indication of shut-down" are to exercise a police function. They are not to promote safety, they are to police the operator. They seem to indicate a distrust not only of the ability but of the integrity of the operator. The first requirement for safe operation is safe operators. After all, there is no need for setting up a system of mechanical policemen because, if the operator wished, he could shut off the fan and its policeman just as he could shut off the fan if it had no policeman.

The proposed schedule requires "check valves or equivalent devices" in pipes connected to tanks. A pipe through which liquid is removed from a tank obviously cannot be equipped with a device which will prevent liquid from flowing out of the tank through the pipe!

In the proposed schedule there is the requirement for "approved" pumps. However it must be said that in my opinion nothing is accomplished by this except the needless expenditure of a considerable sum of money. "Approved" is no indication that the pumps are satisfactory, or safe, or have a hexane-saving seal in place of packing. Unapproved pumps may very well be better than some of the approved ones; and, as a matter of fact, some manufacturers sell the same pump, approved or not approved, with the only difference being the name plate and the cost.

The proposed schedule reads "indicate low pressure in pressurized cabinets or rooms" but should read "indicate no pressure . . ." High pressure is never needed. Pressure, just as long as it is any pressure at all, is all that is needed.

In the proposed schedule there is a "note" applying to several things. It is in the nature of advice rather than an actual part of the schedule. It is suggested that advice be omitted from this and similar instruments for the sake of clarity and simplicity.

The proposed schedule requires "electrical equipment" to be approved for class 1 hazardous locations but allows unapproved "control instruments" if housed in a pressurized cabinet or room. It seems reasonable that unapproved electrical equipment be allowed if it too is housed in a vapor-free atmosphere.

The proposed schedule requires that a pressurized room, if used, be equipped with a pressure gauge and an air lock. It is thought that both are unnecessary and add cost and bother rather than safety. If a room is reasonably well constructed, has a reasonably tight, self-closing door and has a fan blowing hexane-free air into the room, there is no chance of hexane entering the room in quantities that would cause any degree of danger. The flow of gas would be air out of the room rather than solvent vapor in, and that is all that is needed. The fan could be observed to see that it was running just as well as a pressure gauge could be observed. An expensive, fancy set-up is not required for safety.

In connection with the requirement for vapor-proof flashlights, it is my opinion that ordinary flashlights do not constitute a hazard in hexane vapors. Factory Mutual Laboratories and the insurance companies that they represent do not require approved flashlights in solvent plants. Unnecessary requirements detract from the effectiveness of the proposed schedule or any other similar instrument.

Isolation of the plant as required by these proposed rules seems to be more than is reasonably needed. Attention is invited to the fact that the first paragraph of Section B calls for following N.B.F.U. Standard No. 30. This pamphlet No. 30 allows the above-ground storage of class 1 liquid up to 12,000 gal. within 15 ft. of a property line and storage of 50,000 gal. within 25 ft. of a property line where there can be absolutely no control over what goes on beyond that line. Truck-loading racks with buildings for shelter of pumps and personnel may be within 25 ft. of a property line. Paragraph 704 of N.B.F.U. pamphlet No. 30 eliminates open fires and other sources of ignition and requires proper electrical equipment "in buildings, rooms, and other confined spaces in which class 1 liquids are used." This is greatly different from the 50-ft. and 100-ft. restrictions applied in this proposed schedule.

The proposed schedule also specifies that "unloading to conform—N.B.F.U. Pamphlets 30 and 38." Pamphlet No. 38 prohibits locating in closely-built mercantile or residential areas or within 100 ft. of any building. The proposed schedule specifically includes all important solvent plant structures in the 100-ft. spacing. This distance sometimes is impossible to obtain. Sometimes these rules, if followed, would create a hazard greater than the hazard they attempt to avoid. In the case of a given plant, one would comply with the rules by moving the unloading point to an area where it would be impossible to restrict traffic and activity. It is my belief that the safest possible place to unload solvent is in the solvent-plant area. There one has trained personnel, restricted traffic, grounding, gas alarms, and other things that go to make for solvent-plant safety. If a plant is run with safety, it is ridiculous to assume that a tank car can not be unloaded there with equal safety.

In connection with solvent storage tanks wherein the proposed schedule specifies that "solvent . . . tanks . . . if above ground, to be detached not less than 50 feet," attention is again invited to N.B.F.U. Pamphlet No. 30 which will allow 50,000 gal. to be stored in one tank within 25 ft. of a property line. Is it logical so to penalize a solvent-extraction plant in relation to what is expected of other industry?

At many plants operations are conducted behind locked gates. In these plants it was decided long ago that watchmen should not be entering and leaving this property and that it was safer if they just looked through the fence and left the gate locked. This is not "standard watchman service." In a case at hand the insurance carrier agreed that this is the safest procedure. Therefore one should not allow, let alone require, "standard watchman service." Many operators prefer safety to rules!

The proposed schedule discusses the conforming of approved automatic combination deluge and water-spray protection according to the requirements of N.B.F.U. pamphlets 13 and 15, except 13 and 15 are not enough! There are other requirements. I shall not attempt to go into this phase of the schedule for this in itself requires a long, technical study. I will say I am in disagreement with some of the requirements of the two pamphlets mentioned as well as the special requirements. I am particularly struck with

the fact that requirements are being thrust upon us that are far in excess of those applied to other industries with similar hazards. Refineries have no such rules, natural gas plants have no such rules, nor do dry cleaners or butane dealers or tank trucks or railroads. I think a solvent plant is safer than many filling stations where gasoline may be dispersed by a cigar-smoking attendant to a customer who has no hesitation about lighting a cigarette or flipping a cigarette butt out of the car window, where an automatic cut-off nozzle is used that frequently sloshes gasoline on the ground near a tank truck unloading gasoline. Cars and people in unlimited number go in and out of the danger area at will.

In view of the foregoing, it might be said, in closing, that these requirements seem unnecessary and unjust. Particular objection is taken to the use of such words and phrases as: "competent personnel experienced in . . . hazards of flammable liquids," "adequately curbed and drained," "adequate system," "properly detached," "approved," and "properly located."

Each of these words and phrases may have a different meaning to each person who reads them. And objection is made to the distrust evidenced in the proposed schedule where a mechanical policeman is set to watching the operator with another mechanical policeman watching the mechanical policeman.

Furthermore objection is made to the setting up of the N.B.F.U. pamphlets as rules with the only exceptions being those where adequate requirements are set aside in favor of other more-than-adequate requirements. In at least one case the requirements of the N.B.F.U. are doubled in this schedule.

My final thought is that the solvent-extraction industry should not be burdened with requirements far greater than those imposed on other industries with similar hazards.

The Determination of Pyrophosphate in Commercial Triphosphate

HERMAN J. WEISER JR., The Procter and Gamble Company, Cincinnati, Ohio

ONE OF THE MOST SERIOUS NEEDS in the field of phosphate chemistry has been for a direct, accurate method of determining pyrophosphate in the presence of large amounts of triphosphate. Good methods have been published for ortho- (10) and triphosphate (17), but a procedure for pyrophosphate in commercial triphosphate was needed. Two procedures involving zinc precipitation have been published. The first (1, 2, 5) involves precipitation of the zinc pyrophosphate at pH 3.8 and separation of the precipitate by filtration, followed by ignition and weighing of the precipitate. This is based on the earlier work of Britzke and Dragunov (3). In the second method (15) both pyro- and triphosphate are precipitated as zinc salts; and after drying and weighing, the precipitate is analyzed for zinc. Solution of simultaneous equations gives values for both pyro- and triphosphate. The first method has given good estimates of the pyrophosphate content of some samples despite radiochemical data (12), showing that it may be contaminated with a significant amount of triphosphate. When the pyrophosphate content is less than 10%, there is often no precipitation (12) unless extra pyrophosphate is added (2). As the authors of the second method point out (15), the zinc determination must give very accurate values, or it will adversely affect the pyro- and triphosphate results.

The earliest direct method of determining pyrophosphate was by x-ray diffraction (14, 9). Of course, this method can only be applied to solid samples, and all the pyrophosphate must be crystalline. A method involving the isotope dilution technique (13) also is specific for pyrophosphate. This method requires equipment to carry out the radiochemical counting and an elapsed time of one to three days to complete a determination.

Probably one of the earliest attempts to separate the individual phosphate species by ion exchange chromatography was carried out by the author (16) in 1950–51. The approach was empirical, yielding a separation of ortho- and trimetaphosphate from pyro- and triphosphate. The mathematical approach of Beukenkamp, Reiman, and Lindenbaum (4) proved more fruitful, and they have devised a procedure for separating not only these four species from each other but also the tetrameta- and tetraphosphate (8, 11). Paper chromatography has also been applied successfully to the separation and determination of the phosphate species (7). Both of these procedures have the important advantage of separating the various phosphate species from each other before hydrolyzing the individual components to orthophosphate and determining the amount present by an accurate colorimetric procedure. Since the ion exchange procedure appeared to be capable of greater accuracy by virtue of the larger amount of sample handled, it was applied to the analysis of commercial triphosphate.

DEVELOPMENT OF THE METHOD

Elution Curve. Commercial triphosphate normally contains 5 to 15% pyrophosphate and 85 to 95% triphosphate (17). Because of the great difference in the amounts of these two species it was necessary to modify the elution procedure of Peters and Rieman (11) to insure their quantitative separation. In addition, it was found that the acid eluant of Higgins and Baldwin (6) provided such a superior separation of ortho- and pyrophosphate that it was incorporated into the method. In fact, the separation was so good that it was necessary to add KCl to the eluant and change to eluant No. 2 before the end of the fraction so that the fractions would not be too widely separated. No evidence was obtained