General Safety in Handling Solvents[1]

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Abstract

There are two major requirements for safety in plant operations: 1) convince everyone that it is smart to be safe, and 2) make it easier to be safe than unsafe. The most important method of instituting a workable and reliable safety program is that the general safety philosophy must be truly believed by management and promoted by them. It is only in this atmosphere that plant personnel will be able to progress to an outstanding safety record. The procedures for safer plant operations and general safety is a continuing program, and must be reviewed and revised, when required, in order to enhance safer operations.

Introduction

IN THE OFFICE BUILDING of a nearby chemical plant, a sign lists the order of concern of the company's management for safety, production, costs, quality and profit. At the top of this list is safety. The attitude of a company's management is the first step in industrial safety. This is true since basically it is easier for an individual to be unsafe than safe. The prudent action in a challenging situation at home, on the highway or on the job does not frequently appear except as hind sight. It is managements job to show that safety is smart and that it is easy. Money spent wisely to do this has an exceptionally high value measured economically or humanly. Safety demands the efforts of employees from the top down. Focusing these efforts in an effective program is a real challenge. The principles that apply to our plant's operations and to much of the petroleum industry are equally applicable to the chemical oil industry, whether we discuss workmen, procedures, or equipment. At Baytown, as in practically every plant, we support a plant safety program, under a Safety Department, which is geared to the improvement of our employee's attitude and working habits. In addition, our efforts are directed toward constructing safe equipment and specifying safe operating procedures. Our discussion this morning concerns our procedures for safer plant operations and general safety.

In addition, I have been asked to discuss safety in handling solvents, and in particular, hexane. Over the years, we have probably handled more barrels of solvents safely than any other company. Of course, we have made a few mistakes, including one involving use of a wrong hose for xylene last month. However, a discussion of our general safety program might be of interest, since it can be applied to any industry. With us, safety is the personal responsibility of everyone. Our organized programs involve both employees' attitudes, as previously mentioned, and operating procedures. The rules, procedures and codes are compiled through exchange and accumulation of information in our plant, in our company and in the industry.

The rules by which solvents are handled have their roots in the experience in our industry dating from 1936 (approx). In order to formulate rules for handling solvents, consideration is first given to the physical properties of the product; then to the application of these properties to the type of equipment and corresponding operating procedures. The petroleum industry is concerned primarily with avoidance of fires. For ignition to occur, the fuel must be vaporized, mixed with the right amount of air, then ignited by means of heat or flame. Therefore, the most important property of a solvent to consider is its flammable range. Another is the autoignition temp. Actually, handling hexane is very little different (if any) from handling gasoline. As shown in Table I, the autoignition temp for cottonseed oil is 650F, and for hexane it is ca. 480F, while some of the other hydrocarbons are above 1,000F.

TABLE I

Auto-Ignition Temperatures of Flammable Liquids and Gases

Name	Auto-ignition temp., °F
Benzene	1076
Butane-N	806
Butane-i	1010
Cottonseed oil	650
Ethane	950
Ethylene	1009
Heptane-N	452
Hexane-N	477
Hydrogen	1076
Kerosene	490
Linseed oil	820
Lubricating oil	700
Methane	999
Pentane-N	588
VM and P Naphtha	450–500

Speaking for myself, I'm not sure that these differences are significant, except to indicate trends. For example, ignition of oil leakage on hot compressors and other equipment at 650F is fairly common. Further, steam lines at 625F have been found to ignite hydrocarbon, particularly where insulation has been oil soaked. Ethylene has a higher autoignition temp than ethane. However, the fact that ethylene has a wider flammable range is of greater consequence. As ethylene spreads from a leak toward a source of ignition, it is more likely to be of the right mixture for ignition. Hydrogen has a very wide flammable range, but also requires very low energy for ignition. It is more hazardous than any hydrocarbon because of this.

A low autoignition temp for hexane would indicate that slightly more emphasis should be placed on the location of hexane pumps. They should be distant with respect to other equipment and steel load-bearing structure. In addition, consideration should be given to the installation of fixed fire protection. In one location at our plant, hexane pumps operating in a congested area at 300F and 60,000B/D, are equipped with automatic block valves and an automatic spray water deluge system. Despite good pump maintenance, the installed equipment has prevented several (what may have been) nasty fires. In other locations, operating at lower temp, rates, in less congested areas, no fixed fire protection is usually provided for such stocks. Design consideration for installation of safety facilities is an important part of our safety program, and will be discussed subsequently.

A difference between hexane and gasoline is its range of flammability. In general, gasoline-air mixtures encountered in process operations are too rich for ignition. Mixtures of the right concn for ignition are found as a result of a leakage of gasoline outside the equipment or admission of air to the equipment internals on startup or shutdown. Hexane within a tank or vessel is also too rich for ignition; however, at low atmospheric temp, flammable mixtures can be encountered in storage or in equipment open to the air.

Figure 1 presents the approx relationship of temp and flammable range for common solvents. It assumes that the tank and its contents are at the same temp. If this is not the case, the flammable range will be shifted. If any of the fuel is at a temp within the range, a flammable mixture can result. Further, contamination with a lighter product or a heavier one can move the liquid into the flammable range. A mixture of a liquid which is too rich with another too lean can be flammable. For example, switch loading of gasoline (too rich) and kerosene (too lean) is avoided by refiners. A number of accidents involving tank truck operations have occurred because of the flammable range shift of gasoline-kerosene mixtures. As a general rule, if a solvent

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TABLE II

Disabling Injury Frequency

Year	Humble, Baytown	NSC rank[a]
1959	0.73	1
1960	1.62	8
1961	1.72	6
1962	1.25	3
1963	1.48	4

[a] Large refineries.

TABLE III

Duties of the Refinery Safe Operations Committee

1. Review engineering design and plant layout.
2. Review operating procedures.
3. Coordinate operating equipment inspection.
4. Review accidents and near accidents.
5. Develop procedure for handling flammable materials.
6. Distribute information concerning safe operations.
7. Recommend appropriate action.

is too lean and is mixed with another solvent which is also too lean, the mixture will be too lean. Similarly for two solvents, both too rich. But if one is too rich and one is too lean, be prepared for trouble.

Considering hexane, note that the flammable limit is too rich above temp of 35F. For mixtures at ordinary temp, the flammable range would be expected for those cases where hexane was only present in small concn in oil or seed. VM&P naphtha represents a more serious situation because of its flammable range between 50 and 120F, temp which are normally encountered. Note that heptane is very close to turbo fuel No. 4 for which elaborate rules have been prepared in the oil and aircraft industries. Figure 1 points out the necessity of being aware of handling conditions and the characteristics of the stocks—the temp at which a stock is flammable is important to us and most certainly affects the methods and handling the stock. Certainly, determination of the characteristics of mixtures over a process concentration range would be important to us.

In refining operations, we are very aware of the processing environment, and have developed rather elaborate rules governing handling of hydrocarbons which can be in the flammable range. We avoid this range by changing process conditions (temp) if possible. If this is not possible, an inert atmosphere is generally employed. Solvents handling and processing operations are conducted under strict rules and procedures to minimize the hazard and to prevent conditions which could cause ignition of flammable mixtures. These rules are based on our own experience plus similar API and other guide lines. In addition to those responsible for equipment operation, safety in our plant is a concern of a safe operations committee. The work of this group supplementary to other formal safety programs, has contributed to an improved safety record as shown on Table II.

Over the last 13 years, the average disabling injury frequency rate for the Baytown Refinery has been 1.5/M man-hr. For the last five years, the industry average has been ca. 5. Looking at Table II, our average rank with respect to large refineries is ca. 4. However, each year the same refineries are not in the list of the top 10 with the possible exception of our refinery at Baton Rouge. So Baytown's position is probably 1 or 2. In compiling this record, we have supported the efforts of our company and the API. The oil industry has dropped the disabling injury frequency rate from ca. 50/M man-hr worked to ca. 5.

Safety procedures in use today with respect to emphasis on operations had their beginnings on an inter-plants basis in 1947. This effort has now evolved into a clear responsibility for safety throughout the organization. However, a safe operations committee activity has substantially increased the emphasis on safety. As shown on Table III, the duties of the refinery safe operations committee is as follows:

1) Review engineering design and plant layout of new units and changes to existing units. Does the equipment conform to the prescribed layouts? If there is congestion, is addition fire protection necessary?

2) Review operation procedures. Are all the important points covered? Are emergencies fully considered?

3) Coordinate equipment inspection of operating facilities and evaluate results. This will be discussed in more detail.

4) Review accidents and near accidents. Accidents from our refinery, company and applicable incidents in the industry are reviewed from the standpoint of procedure, design or equipment.

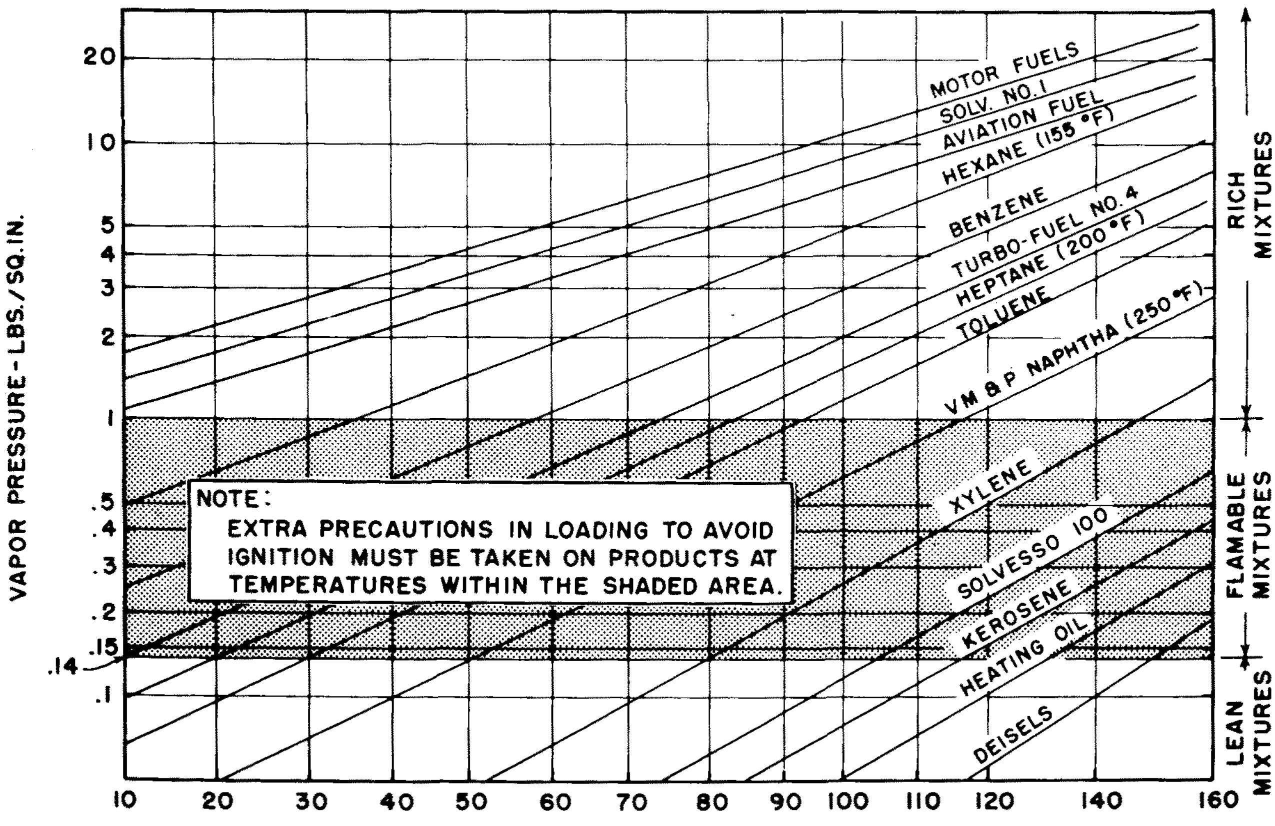

Fig. 1.

TABLE IV

Guide for Unit Safety Inspection

A.

1. Access Ways
   Congested area? Passage blocked?
2. Emergency Blowdown, Flare systems
   Winterized? Discharge location?
3. Control Room
   Hydrocarbon entry? Information?
4. Electrical
   Sealed? Conduit deteriorated? Identification?
5. Fire Protection
   Winterizing? Location?
6. General Area
   Warning signs? Procedures? Housekeeping?

B.

7. Machinery
   Leaks? Vibration? Safety devices?
8. Piping and Pipe Supports
   Insufficient supports? Idle piping?
9. Training
   Emergency Procedures?
10. Structure
    Appearance? Fireproofing?
11. Safety Valves
    Records? Car seals?
12. Vessels and Exchangers
    Hot spots? Leaks? Insulation?

5) Develop guides for safe handling of flammable materials, coordinate test programs. Provide new or supplementary information concerning new products, equipment or problems.

6) Distribute information concerning safe operations. Information distributed to appropriate individuals.

7) Recommend appropriate action. Sometimes we're in the middle. Recently, looked at similar system costing several thousand dollars. Found that, in event of fire, we would have 36 min before failure at full pressure. Could correct in ca. 10 min. Reasonable safety factor.

The principal function of the committee is to promote and stimulate safe operation of the refinery equipment through membership composed of representatives from the operating divisions, maintenance, engineering and safety. Normally, committee members have 15–25 years of service and wide refinery experience. The work of the committee has improved safety as a direct result of consideration by them and suggested changes to many projects. In addition, the committee members have increased emphasis on safety within their division. In many cases, deliberations by the safe operations committee have resulted in changes which are adopted to meet refinery-wide needs ranging from sewer capacity to gasket specification.

Our employees are capable, and they are well trained. Each does a good job in all the little details necessary to accomplish an efficient operation. However, after a time, they may get used to the little noises and bumps, which usually exist. One of the contributions of the safe operations committee has been to sponsor a formal safety inspection program, from which many benefits have accured. We find that a safety inspection about once a year assures that the unit stays in peak condition with respect to safety; it reminds the operators to look at all the bumps to pick out the new ones, and to listen closely to the noises. The inspection is conducted by a supervior from another division as well as by the supervisor of the inspected unit. A manual informs the operator, and inspector, of the consideration which apply for installation and provision of safety equip-

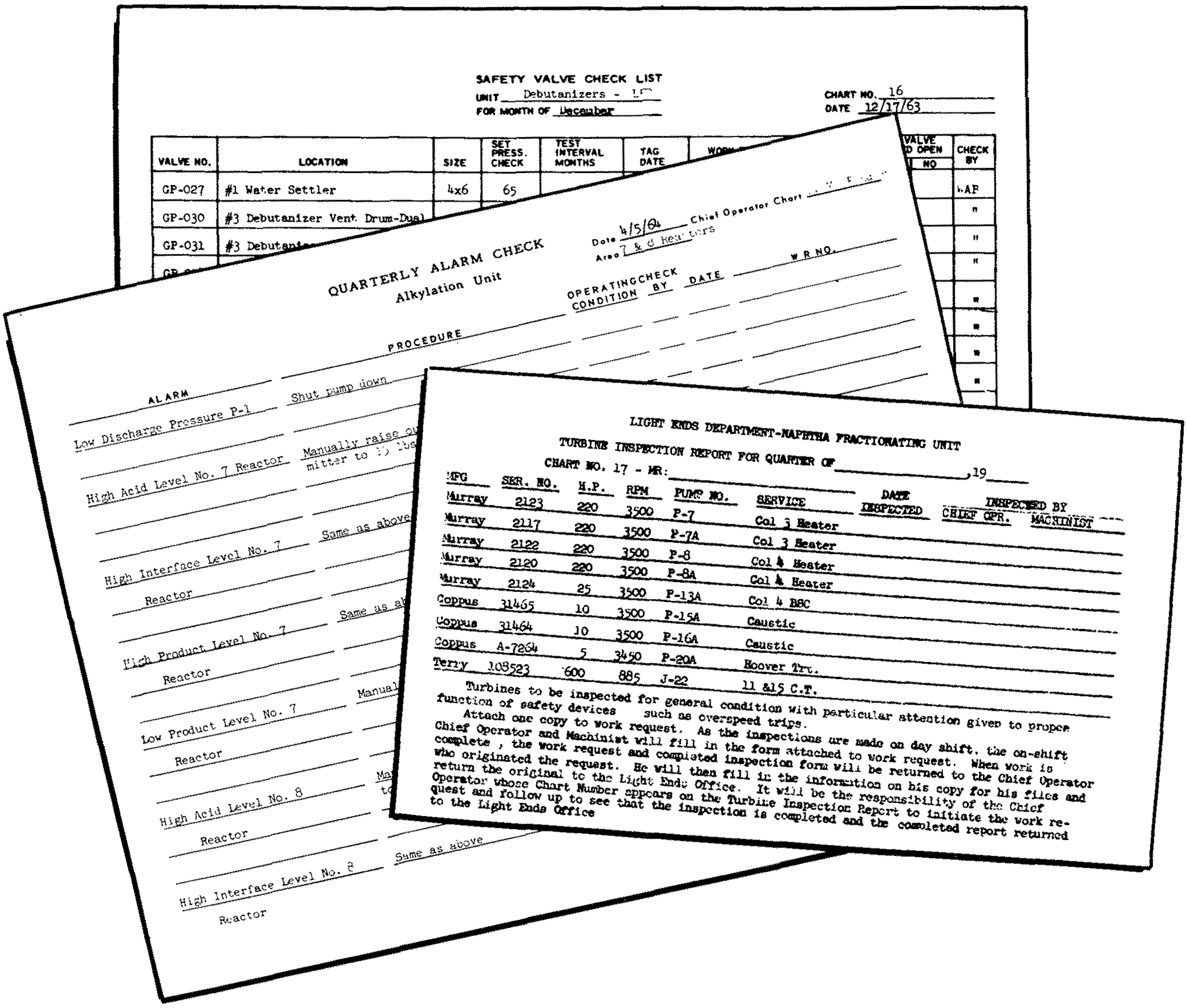

FIG. 2

ment, and for material selection and construction principles. The basis for the manual is primarily published practice guides from the API and our Technical Division.

A summary of the inspection check list is presented on Tables IV (A and B). Inspection of a major unit such as a 80,000 B/D pipe still requires ca. one full day.

(1) *Access Ways*
Is area open or congested?

(2) *Blowdown, Flare and Pumpout Systems*
Is it evident that systems are adequate? Have changes occurred? Are emergency automatic operators tested? Identification?

(3) *Cooling Towers*
What is the general mechanical conditions?

(4) *Control Room*
What is condition of required records? Is there any entrance for hydrocarbon? Are emergency drills conducted?

(5) *Electrical*
What is condition of conduit and equipment? Identification?

(6) *Fire Protection*
What is condition of fixed equipment? First Aid?

(7) *Furnaces*
What is appearance of firebox? Flame or gas safety devices?

(8) *General Area*
Is there debris? Subway gradings?

(9) *Machinery*
What is maintenance level? Lubrication?

(10) *Piping and Pipe Supports*
Are there temporary supports? Excessive vibration? Sufficient supports?

(11) *Procedure for Training*
What is status of operating and emergency procedures? Drill records?

(12) *Structure*
What is appearance of paint? Metals? Handrails?

(13) *Safety Valves*
Are records up to date? Car seals in place?

(14) *Sewers and Oil Recovery*
Are sewers adequate? Is skimming equipment in good condition?

(15) *Vessels and Exchangers*
Is there evidence of hot-spots? Stressed piping? Deteriorated insulation? Leakage?

(16) *Other—Pump slabs, loading racks, docks, tankage, transportation and portable compressors, manlifts, etc.*

Previously, safety inspections had been conducted less formally and required about two hr. Generally, the inspection determined only whether or not good housekeeping practices were being followed. Having a manual which describes what to look for, a check-off sheet, and a full day to do the work assures that a thorough inspection is accomplished. Further, each supervisor who participates learns something concerning his own unit's safety.

The average inspection report will require four pages of material. Most of the items will report good condition of the equipment. Even if nothing of consequence is found, the inspection would be worthwhile. Actually, finding nothing has never been the case. Even considering our 1.5 million man-hr disabling injury frequency rate, there is always something which can be improved. In some cases, the need for additional or modified pipe supports on piping from 0.5 to 24 in. was uncovered. Procedures for handling emergencies have been improved and will be improved still further. Fire monitor nozzles were found with obstructions to their proper field of coverage and with defective locking devices. Empty and partly empty first aid extinguishers were found. Many more small maintenance items were found from housekeeping to insulation. Most of the deficiencies can be eliminated through improvement in the daily operating and maintenance procedures employed at our units. Our present effort is expected to improve this. Future formal inspections will be held on an annual or biannual basis. These should uncover less as a result of implementation of better procedures, and because of informed people through an operations safety as to what is expected.

TABLE V

Weekly Basic Equipment Safety Inspection

Scott air pak and cannister masks
Goggles
Eye fountain and safety shower
Stretcher
Ladder
Fire extinguishers and hose reels
Fire monitor and automatic sprinklers
Warning signs (H_2S, thermal expansion, etc.)
Turbine emergency start-up and pump out
Safety va.ve stacks
Stairways—Railings
Leaks (oil, steam, water, chemicals)
Permit tags

Note: Inspection to be performed on 7–3 Shift each Saturday or Sunday.

Increased emphasis has been placed on equipment checks by our operators. Through the years, we have learned through experience to check safety valves, overspeed devices on turbines and shutdown devices or alarms. These checks are made either monthly or quarterly by operators or mechanics and each operator is responsible for certain equipment. Records are kept of the condition and required maintenance is performed as a result of the inspection. Compliance with these procedures has been improved. Fig. 2 shows typical safety valve, turbine inspection and alarm check lists. Note that the position of the block valve associated with safety valves is recorded. In some cases, a valve is installed which is necessary for isolation of equipment, yet must be kept open while in operation. Such a valve is listed on the safety valve check sheet. Alarm test procedures are spelled out. In some cases, alarms and automatic shutdown devices may be actuated. Procedures must be spelled out to avoid shutdown, yet tests must be conducted to assure operation when needed. Experience has shown that tests of alarms each three months will pick up a small percentage of bad-order instruments, and at present this frequency is employed on most alarm devices.

Most of our units have been conducting weekly checks of the condition of our personal protection equipment and fixed fire protection. This effort has simply been intensified because of finding many deficiencies as a result of the safety (audit) inspections. As shown on Table V the check list covers such items as gas masks, eye fountains, fire equipment, warning signs and housekeeping. As a simple example, we hope to avoid a recurrence of an operator picking up a hand extinguisher at ground level to find it empty on the seventh floor of a catalytic cracking unit. Most of our units now post sketches of fire extenguisher locations, and can recite them from memory.

A benefit which accrues to any program which increases emphasis on safety is the improvement in attitude of the employees who operate our units. Once they know something of the general principles involved in operating safety and have developed routines and procedures for their own units, we have learned to expect a considerable improvement in general safety. Increased emphasis has paid dividends for us, and I believe it will for you. It may even convince you it's smart and also easy.

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