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COATINGS AND THEIR SAFE APPLICATION

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There is no doubt that there are definite hazards in the application of coatings to the interior of closed spaces such as are found aboard ship. The use of synthetic resin coatings for specialty linings aboard ship has greatly increased the number of areas where coatings are used. These linings have become necessary due to the many new chemical ladings now transported. This in itself tends to multiply the frequency of possible accidents. That the hazards in applying coatings are real is demonstrated by the fact that there have been several fatal accidents in the last fifteen years.

On the other hand the safe use of hazardous materials is dependent upon the economic need for the product. If this need justifies the precautions and protective equipment required to maintain safe application conditions, then proper safety methods can be developed which reduce the hazards involved.

There are two excellent industrial examples of this: one is the explosive industry, and the second is the development and use of atomic energy. In both of these areas safety precautions were developed which reduced the hazards of working with difficult materials to an absolute minimum. The marine industry, particularly the tanker or petroleum transportation division, has also maintained very high safety standards due to the handling of many flammable and explosive liquids.

The coating hazards we are concerned with here, however, do not involve the tanker operators since once the coatings are applied, they actually reduce the possibility of fire or explosion by providing a surface coating which is easily gas-freed. The surface coating does not accumulate and retain hazardous liquid or fumes such as is the case where heavy rust films are built up on unlined tanks.

The potential hazards exist then in the shipyard or where the enclosed spaces in ships are being coated such as in drydock or along outfitting docks. In the last few years the transportation of chemicals by tanker has increased manifold. Many of these chemicals are corrosive or require coatings to prevent contamination from iron or iron oxide. Such materials are the ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; aromatic solvents such as toluol and xylol; jet fuels, glycols, caustic solutions, wine, sugar, syrups, alcohols, and many similar products.

The tankers being built today require linings even for gasoline and other refined petroleum products, and many different coatings are used which were unknown to the marine industry a few years ago. By the use of these linings not only is the corrosion to the interior of tanks decreased, but the quality of the products is maintained at refinery standards.

Coatings such as vinyls, saran, epoxies, polysulfides, phenolic epoxies, and inorganic zinc coatings are now commonly applied, and each type of coating has its own characteristics. These are primarily applied to the interior of tanker tanks although there are other enclosed spaces aboard ship which also require coatings. Chain lockers, deep wells, void spaces, and double bottoms all use coatings which can provide difficult safety conditions. Alkyds, coal tar, and asphalt cutbacks are common in these areas.

The following table lists some of the characteristics of commonly applied coatings which bear on their safe application. It will be noted that the MAC (Maximum Allowable Concentration) of all listed except the inorganic zinc silicate is in the range of 100 to 500 PPM. This indicates that from a health standpoint all organics are approximately equal and that protective equipment must be used for the application of all in confined areas.

Once it was realized that there was a greater and greater need for coatings and linings in industry and the marine fields, a research program was established at Battelle Memorial Institute in Columbus, Ohio, to develop methods for the safe application of coatings in enclosed areas. The aim of the program was to determine a practical method

TABLE I

Characteristics of Commonly-Applied Coatings

Type	Resin	Solvents	Flash Point Open Cup	Explosive Limit	Solvents	Toxicity Resins
Vinyls	High molecular weight chlorinated hydrocarbons self-extinguishing	Ketones and aromatics	30—100°F	1.3 to 1.8	100 MAC	Nontoxic
Saran	High molecular-weight chlorinated hydrocarbons self-extinguishing	Ketones and aromatics	0—70°F	1.3 to 2.0	200 MAC	Nontoxic
Epoxies	Will support combustion	Ketones and aromatics	30—95°F	1.3 to 1.8	100 MAC	Some cause dermatitis in sensitive individuals
Asphalt Gilsonite Cutback	Will support combustion	Aliphatic or aromatic petroleum	100°F +	1.1	200-500 MAC	Nontoxic
Coal Tar Cutback	Flammable	Aromatics	40—100°F	1.1 to 1.27	200 MAC	Severe skin irritation
Alkyds	Flammable	Aliphatic or aromatic petroleum	100°F	1.1	200-500 MAC	Non-irritating
Inorganic Zinc Silicate	Inorganic silicate non-flammable	Water	None	None	—	Silicate mildly alkaline Limited skin irritation

of application of these coatings with simple rules that any painter or applicator could understand and easily follow from written instructions. By following these rules, the applicator could be certain that no explosion could occur and this fact was to be proven by Battelle's tests.

The hazards found in the application of coatings in enclosed areas can be placed in three classifications:

1. Danger by fire or explosion.

2. Damage to the applicator from inhalation of the various solvents used in the coatings.

3. Dermatitis caused by contact with resins or solvents used in the coatings.

The starting point in the test program was the determination of the lower explosive limit not only of the individual solvents but of the combined solvents as they were used in coatings. The lower explosive limit of the individual products could be obtained from literature; however, little or no work had been done on the explosive limit of combined solvents to determine whether a greater or lesser hazard existed from these mixtures.

The lower explosive limit of any solvent or combination of solvents may be defined for the purpose of this paper as the amount of solvent vapor in air which is just below the point at which an explosion will occur if the air and solvent mixture is ignited with a spark. This lower explosive limit of the air and solvent mixture is extremely important in a safety study because if the lower explosive concentration of solvent in air is not reached, then no explosion can occur. While flash point is often a more common point of reference for safety than explosive limits, the lower explosion limit figures are more important in a safety program dealing with coating application since the primary means of maintaining safe application conditions is through ventilation. Part of the program at Battelle was to develop a piece of laboratory apparatus from which reproducible results could be obtained for the explosive limits of both individual solvents and solvent mixtures used in coatings.

The following two tables show the lower explosive limit developed by the above apparatus for individual solvents which are used in various coatings as well as for combinations of solvents which are typical of specific types of coatings:

TABLE II

Test Explosive Limit Data for Individual Solvents

Material	Spark-Explosion Limit, % Vapor by Volume in Air	Pressure mm Hg	Temperature °F
Ethyl Alcohol	3.31	760	77
Isopropanol	2.50	760	77
n-Butyl Alcohol	No limit found	665	122
Tetrahydrofurfural Alcohol	No limit found	743	122
Acetone	2.55	760	77
Methyl Ethyl Ketone	2.15	760	77
Methyl Isobutyl Ketone	1.80	760	77
Cyclohexanone	1.49	760	122
n-Butyl Acetate	1.57	760	122
1-Nitropropane	2.32	760	122
Xylol	2.24	760	122
Aromatic Petroleum (toluol range)	1.19	760	122
Aromatic Petroleum (xylol range)	1.28	760	122
Petroleum, Naphthenic fraction	No limit found	526	122
Mineral Spirits	1.10	760	109

TABLE III

Test Explosive Limit Data on Mixed Solvents

Material	Spark-Explosion Limit, % Vapor by Volume in Air	Pressure, mm Hg	Temperature, °F
Ketone Aromatic Thinner	1.13	760	82
Ketone Aromatic Cleaner	1.65	760	86
Wash Prime Solvents	1.38	760	86
Vinyl Tank Lining Solvents	1.40	760	86
Vinyl Boottopping and Topside Solvents	1.25	760	77
Asphalt Gilsonite Solvents	No limit found	760	122
Epoxy Ester Solvents	No limit found	760	122
Tank Lining Epoxy Solvents	1.48	760	86
Phenolic Tank Lining Solvents	2.40	760	86

It will be noted that the mixed solvents are generally in the same range as the individual solvents. However, they are higher in value than the lowest single solvent and below the highest.

A second step in the study of these methods of safe application of coatings was the determination of actual evaporation rate of the solvents from the individual coatings. While it is easy to visualize the maximum evaporation of solvents at the time of spraying on the surface, nevertheless the coating must be applied as a liquid; and therefore solvents evaporate from the liquid state of the coating over a period of time.

This is an important factor in safety as proven by the fact that accidents have occurred even though proper ventilation equipment was installed during the time of application. In one instance as soon as the coating of the tank was complete, the ventilation equipment was moved from this tank to another to start coating application there. Approximately an hour later a workman laid a piece of steel across the hatch opening and applied an acetylene torch to cut it to shape. The hot metal dropped down into the tank and an explosion occurred immediately. The explosion occurred, of course, as a result of the evaporation of the solvent from the coating during the drying period after application and after the ventilation equipment was removed.

Two charts follow: Chart 1 illustrates a 5-coat vinyl tank lining and Chart 2 shows a 5-coat epoxy tank lining. The evaporation rate for each coat over a period of approximately four hours is shown.

there is no ventilation to dilute the solvent-air combination.

Another factor which must be considered is the density of the solvents compared to air. This is shown in Table V, and in every case it will be noted that the density of the solvent vapor is substantially greater than that of air.

with a very low flash point will have a relatively high lower explosive limit. This is demonstrated by acetone with a flash point of 0°F and a lower explosive limit of 2.15 while turpentine has a flash point of 95°F with a lower explosive limit of 0.8. If the amount of solvent vapor is the

TABLE V

Properties of Flammable Liquids Used in Paints and Lacquers

Name	Flash Point °F Closed Cup	Flash Point °F Open Cup	Explosive Limits % by Volume in Air Lower	Explosive Limits % by Volume in Air Upper	Vapor Density (Air=1.00)	Boiling Point °F
Acetone	0	15	2.15	12.0	2.00	134
n-Amyl Acetate	76	80	1.10	...	4.49	300
n-Amyl Alcohol	91	120	1.20	...	3.04	280
Benzene	12	...	1.40	8.0	2.77	176
n-Butyl Acetate	72	90	1.70	15.0	4.00	260
n-Butyl Alcohol	84	110	1.70	...	2.55	243
Cellosolve	104	120	2.60	15.7	3.10	275
Cellosolve Acetate	124	135	1.71	...	4.72	313
Cyclohexanone	147	...	...	...	3.38	313
Ethyl Acetate	24	30	2.18	11.5	3.04	171
Ethyl Alcohol	55	...	3.23	19.0	1.59	173
Fuel Oil No. 1	100-165	...	...	...	...	...
Gasoline	-50	...	1.30	6.0	3-4	100-400
n-Hexane	-7	...	1.25	6.9	2.97	156
Kerosene	100-165	...	...	...	...	...
Methyl Alcohol	54	60	6.00	36.5	1.11	147
Methyl n-Butyl Ketone	...	95	1.22	8.0	3.45	262
Methyl Isobutyl Ketone	73	...	1.34	8.0	3.45	244
Methyl Ethyl Ketone	20	...	1.81	11.5	2.41	176
Methyl n-Propyl Ketone	...	60	1.55	8.1	2.96	216
Mineral Spirits	100-110	...	1.10	6.0	...	300-400
Naphtha, Coal Tar	100-110	...	...	...	...	300-400
Naphtha, Safety Solvent	100-110	...	1.10	6.0	...	300-400
Naphtha, V.M. & P.	20-45	...	1.20	6.0	...	212-320
n-Propyl Alcohol	59	65	2.50	...	2.07	207
Isopropyl Alcohol	53	60	2.59	...	2.07	181
Stoddard Solvent	100-110	...	1.10	6.0	...	300-400
Toluene	40	45	1.27	7.0	3.14	232
Turpentine	95	...	0.80	...	...	300
o-Xylene	63	75	1.00	...	3.66	291

This indicates in complicated tanks or deep tanks such as are common aboard ship that the solvent will tend to accumulate in low areas and that the explosive limit may be reached in pockets whereas the solvent-air combination in the tank generally would be less than the limit. This point cannot be over emphasized when it is combined with the fact that the solvent evaporation from any of these coatings is governed by time. Even though there might not be sufficient solvent left in the coating to create an explosive condition in the entire tank, it is possible to build up a solvent concentration in a limited area in the bottom of the tank which could be hazardous.

Note also that this chart compares the flash point with the lower explosive limit for the solvent. In many cases the solvent

criteria irrespective of the temperature (and this would have to be assumed in calculating the amount of ventilation required in any given tank) the solvent with the higher explosive limit would be preferable for use in coatings.

All of the information so far has shown that ventilation or dilution of the solvent vapor from the coating is the most foolproof method of eliminating hazards. This is indicated by the statement that if the lower explosive limit is never reached, there can be no explosion. In order to maintain maximum safety, however, it is necessary to properly ventilate tanks since they are usually deep and complicated in structure. Often the practice is to place a blower in a tank opening and to blow air into the area where coating work is taking place.

Generally this is an unsatisfactory procedure if the blower is located at the opening of the tank without an extension trunk. The air is circulated only at the opening and does not move or dilute the air in other portions of the tank.

If a trunk is extended from the blower into other portions of the tank, it tends to create a turbulent condition which again does not remove the solvent from all areas of the tank.

It has proven to be much better procedure to exhaust the air from the lowest portion of the tank, making certain that the openings in the top of the tank are free so there is adequate access of air into the tank. Since the solvent vapors are heavier than air, the air coming in at the top tends to wash down through the tank, carrying the solvents with it, and the maximum concentration of solvents is removed rapidly from the lowest point.

Using the recommended ventilation systems, together with the rate of evaporation and the lower explosive limit of the combined solvents, the following table was made up for various sizes of tanks in which the blower size and the number of air changes per minute are recommended:

TABLE VI

Recommended Ventilation for Various Sized Tanks

Size of Tank	Volume in Cubic Feet	Cubic Feet of Solvent Vapor to Make 1% by Volume	Gals. Coating Used to Make 1% by Volume of Solvent Vapor in Air	Air Changes per Hour Needed to Keep Solvent to 1% by Volume	Gallons of Coating Sprayed In One Hour	Minutes Required to Change Air to Keep Solvent to 1% by Volume	Recommended Suction Fan to Keep the Air Far Below Any Explosive Limit (Cu. Ft. per Minute)	Recommended Changes of Air in Minute to Keep Solvent Fumes Far Below Explosive Limit
5,000 gals.	668	6.7	26	19 20	5	3	1,000 cu. ft.	40 seconds
10,000 gals.	1,336	13.4	.52	9 60	5	6	2,000 cu. ft.	60 seconds
25,000 gals.	3,342	33.4	1.30	3.80	10	8	2,000 cu. ft.	1.7 minutes
50,000 gals.	6,684	66.8	2.60	2.30	10	16	3,000 cu. ft.	2.2 minutes
100,000 gals.	13,378	133.6	5.20	1.30	10	31	5,000 cu. ft.	2.7 minutes
250,000 gals.	33,420	334.2	13.00	0.77	20	60	10,000 cu. ft.	3.3 minutes
400,000 gals.	53,500	535.0	20.80	0.48	20	92	10,000 cu. ft.	5.4 minutes
13,500 bbls.	75,800	758.0	29.40	0.34	60	35	25,000 cu. ft.	3.0 minutes
27,000 bbls.	151,800	1516.0	58.80	0.26	60	70	25,000 cu. ft.	4 3 minutes
50,000 bbls.	280,000	2800.0	108.30	0.14	50	130	50,000 cu. ft.	5.6 minutes

The second hazard found in the application of coatings in enclosed areas concerns damage to the applicator from inhalation of the various solvents in the coatings. It is well known that solvents of all types in paints, varnishes, lacquers, and synthetic resins should not be breathed continuously for extended periods of time as possible harm to individuals can occur. The solvents used in synthetic resin coatings however are no more toxic or anesthetic than many of those used in paints, varnishes, and enamels. This is demonstrated by the following list of solvents taken from *Dangerous Properties of Industrial Materials* by N. Irving Sax, 1957, showing the maximum allowable concentration (MAC) of the various coating solvents based on an eight-hour day exposure.

TABLE VII

Substance	Maximum Allowable Concentration
Acetone	1000
Benzol	35
n-Butanol	100
n-Butyl Acetate	200
Butyl Cellosolve	200
Cellosolve	200
Cellosolve Acetate	100
Ethyl Acetate	400
Ethyl Alcohol	1000
Ethyl Ether	400
Gasoline	500
Isopropyl Alcohol	400
Methyl Ethyl Ketone	200
Methyl Isobutyl Ketone	100
Naphtha (Coal Tar)	200
Naphtha (Petroleum)	500
Stoddard Solvent	500
Turpentine	100
Toluol	200
Trichloroethylene	200
Xylol	200

While the maximum allowable concentration of aromatic hydrocarbons and turpenes such as toluol, xylol, and turpentine is in the same range of maximum allowable concentration as the ketones, they present greater difficulty from a physiological standpoint.

For example, on Page 245 under "Spray Painting" in the *Manual of Industrial Hygiene*, 1944, it is stated that, "The toxicity of the solvents varies from the very toxic benzene to the relatively nontoxic acetone" which is the lowest of the ketones. Also, in Arthur K. Doolittle's The Technology of Solvents and Plasticizers, 1954, it states that, "Ketones and aldehydes are largely devoid of chronic toxicity . . ." In the same section the toxicity of various solvents is summarized in this way: "In summary, chronic toxicity may be expected of benzene and to a lesser extent of other aromatic hydrocarbons, of saturated chlorinated hydrocarbons, many nitrogen compounds, glycol derivates, and carbon disulfide. Other solvents, with perhaps isolated exceptions, injure during industrial exposures almost exclusively as the result of the amount absorbed during one day. There may be some accumulation in the blood due to slow elimination, but there is not the piling up of injury day after day which is the criterion of chronic effect."

In addition the ketone solvents, the primary ones in synthetic resin coatings, are rated as "warning" solvents. There is a characteristic odor from these solvents, and before a dangerous concentration is reached there is mild irritation of the eyes and mucous membrane, warning the workmen to get away from the area before the solvent concentration becomes too high.

The answer to this second safety problem is proper individual ventilation apparatus for each workman applying the coating. There are generally compressed air masks and there are numerous types which supply a continuous volume of clean uncontaminated air to the man applying the coating in the tank. By proper use of such equipment a man may work for several hours in an enclosed area without the inhalation of any of the solvent fumes.

The third problem which may arise in the application of coatings to ships tanks is that of resins which may cause irritation or dermatitis to the skin, particularly when resins come in direct contact with it. This is possible with such products as epoxy coatings, coal tar cutbacks, and phenolic or phenolic epoxy coatings. When such materials are applied, light protective clothing should be used in order to avoid direct contact of the skin with these irritating materials. The irritation may be aggravated when combined with the solvents necessary to form the coating.

A few simple rules have been developed which must be observed in the handling of synthetic resin coatings in enclosed areas. These rules are good practice for the application of any coating in enclosed areas where inflammable solvents are a factor.

1. The first and most important point is ventilation. It must be stressed that adequate ventilation wherever solvents are found is the key to their safe use. This is true whether they are aliphatic hydrocarbons with low toxicity or aromatic hydrocarbons with more dangerous physiological properties. It cannot be over-emphasized that adequate ventilation from either a fire, explosion or health hazard standpoint, is the key to good coating practice wherever these materials are used in enclosed areas.

Ordinarily, no fire hazard will exist if the solvent vapor concentration in air is kept below 1%. This figure is rather empirical however—there is only one solvent in the above list which is below 1% by volume. This is turpentine. The amount of ventilation required in various sizes of tanks to keep the concentration below this limit is shown in Table V.

2. Since the solvent vapors are heavier than air, they have a tendency to concentrate in the lower portions of a tank or closed structure. Therefore, the suction blowers should be operated in such a way as to prevent pockets of solvent vapor being concentrated in the lower portions of enclosed spaces. This can ordinarily be accomplished by sucking the air from the bottom of the tank so that the circulation is from the top manholes or openings down through the tank and up through the blowers. In this way the solvents are swept down and immediately sucked away from the bottom portion of the tank, eliminating any pockets of solvent vapor which might be above the explosion limit.

3. Maintain ventilation in the coated tank until the coating is sufficiently dry so that any remaining solvents cannot build up to the explosive limit. See Table IV.

4. The fourth precaution to be observed is the use of spark proof and explosion proof equipment. Electrical equipment and lights should be explosion proof; tools and shoes shall be spark proof. The use of such equipment has been common practice in the application of synthetic coatings for a number of years.

5. All smoking, matches, fire, flames, or torches shall be prohibited within 50 feet of the area where coatings are being applied.

6. All men working in enclosed areas should wear compressed air type masks to supply them with a flow of clean air at all times.

7. Where epoxies, epoxy coal tar, coal tar or phenolic resins are applied, protective clothing should be worn to eliminate contact with the liquid coating.

If these simple rules are followed during the application of any coating to enclosed spaces, the hazard from fire, inhalation of fumes or contact with the liquid should be maintained at a level which will provide maximum safety to the individual workman.

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VENTILATION FOR HEALTH HAZARDS CONTROL IN THE CONSTRUCTION AND REPAIR OF SHIPS

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Shipyard ventilation prior to World War II was usually limited to locations where the heat stress upon men due to the high ambient temperatures and additional radiant heat could interfere with their productivity. During and subsequent to the war, however,