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MIXED WASTE CHEMICAL COMPATIBILITY WITH PACKAGING COMPONENTS *

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ABSTRACT

In this paper, a chemical compatibility testing program for packaging of mixed wastes at will be described. We will discuss the choice of four γ-radiation doses, four time durations, four temperatures and four waste solutions to simulate the hazardous waste components of mixed wastes for testing materials compatibility of polymers. The selected simulant wastes are (1) an aqueous alkaline mixture of sodium nitrate and sodium nitrite; (2) a chlorinated hydrocarbon mixture; (3) a simulant liquid scintillation fluid; and (4) a mixture of ketones. A selection of 10 polymers with anticipated high resistance to one or more of these types of environments are proposed for testing as potential liner or seal materials. These polymers are butadiene-acrylonitrile copolymer, cross-linked polyethylene, epichlorhydrin, ethylene-propylene rubber, fluorocarbon, glass-filled tetrafluoroethylene, high-density poly-ethylene, isobutylene-isoprene copolymer, polypropylene, and styrene-butadiene rubber. We will describe the elements of the testing plan along with a metric for establishing the resistance of the packaging materials to radiation and chemicals.

I. INTRODUCTION

The purpose of hazardous and radioactive materials packaging is to enable these materials to be transported without posing a threat to the health or property of the general public. To achieve this aim, regulations have been written establishing general design requirements for such packagings. While no regulations have been written specifically for mixed waste packaging, regulations for the constituents of mixed wastes, i.e., hazardous and radioactive substances, have been codified. The design requirements for both hazardous [49 CFR 173.24 (e)(1)][1] and radioactive [49 CFR 173.412 (g)] materials packaging specify packaging compatibility, i.e., that materials of the packaging and any contents be chemically compatible with each other. Furthermore, Type A [49 CFR 173.412 (g)] and Type B (10 CFR 71.43)[2] packaging design requirements stipulate that there be no significant chemical, galvanic, or other reaction between the materials and contents of the package. Based on these requirements, the point can be made that a Chemical Compatibility Testing Program[3] is the means to assure any regulatory body that the issue of packaging compatibility towards hazardous and radioactive materials has been addressed.

II. EXPERIMENTAL

Material properties that should be evaluated to assess the applicability of potential seal and liner materials in mixed waste packaging designs are mass and density changes, permeability, hardness, modulus of elasticity, tensile strength, elongation, compression set, and stress cracking. In this section, we describe the experimental aspects of a chemical compatibility testing program. However, before discussing the testing program itself, a description of the simulant mixed waste forms and of the selected plastics need to be made.

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Four simulant mixed waste forms have been selected. These consist of an aqueous alkaline simulant tank waste, a chlorinated hydrocarbon mixture, a simulant scintillation fluid, and a ketone mixture. The aqueous simulant consist of 179 g sodium nitrate, 50 g sodium nitrite, 82 g sodium hydroxide, 32 g sodium carbonate, 17 g cesium chloride, and 16 g strontium chloride dissolved in 1 L of deionized water. The chlorinated hydrocarbon simulant consists of a mixture of 500 mL trichloroethylene, 250 mL chlorobenzene, 240 mL carbon tetrachloride, and 30 g cerium(III) 2-ethyl hexanoate. The simulant scintillation fluid consist of a mixture of 333 mL toluene, 333 mL xylene, 323 mL dioxane, and 1 mL water. The ketone mixture consists of a mixture of 600 mL methyl ethyl ketone (MEK), 390 mL methyl isobutyl ketone, and 30 g cerium acetyl acetonate hydrate.

Ten plastics having a known chemical resistance to the previously described classes of chemicals were selected. These selected plastics were butadiene-acrylonitrile copolymer, cross-linked polyethylene, epichlorhydrin, ethylene-propylene rubber, fluorocarbon, glass-filled tetrafluoroethylene, high-density polyethylene, isobutylene-isoprene copolymer, polypropylene, and styrene-butadiene rubber.

A. Screening Studies

Since the measurement of all the above mentioned material properties may be costly and time-consuming, screening tests using relatively severe exposure conditions such as high temperatures and high radiation levels can quickly reduce the number of materials being possibly subjected to the full complement of evaluation parameters. The evaluation parameters used in the screening study consist of specific gravity changes in liners and changes in permeability of seals. These parameters are evaluated using standardized test methods such as those developed by the American Society for Testing and Materials (ASTM). For specific gravity changes, ASTM D792[4] is used. In evaluating permeability changes, ASTM D814[5] is used. A reduction in the number of materials requiring more complete evaluation is dependent on some of the materials not passing certain acceptance criteria. These criteria and the rational for their selection will be described in detail in section III.

1. Sample Preparation. Standardized test methods are used to condition, cut, and test the materials. The specific geometry of the material samples is given by the test method. For conditioning of plastics, ASTM D618[6] recommends testing at a standard temperature 23°C (73.4°F) and humidity (50%). However, since it is not be possible to maintain such an atmosphere during testing, it seems expedient to condition samples only at the standard temperature. Thus this all specimens are stored at 23°C for 24 hours prior to the exposure process.

2. Irradiation Exposure. To prepare for radiation compatibility screening testing, the pre-cut liner and seal samples are first exposed to gamma radiation from a ^{60}Co source at SNL. The samples are placed in a stainless steel canister that is continuously purged with air. The canister is lowered into the irradiation pool and brought to thermal equilibrium at 60°C. Once thermal equilibrium has been obtained, the canister is lowered into its irradiation location in the pool. The highest dose rate available at the Low Intensity Cobalt Array (LICA) Facility is 250 kR/hr. Thus for the screening study where a gamma dose of 286,000 rad is required, the samples are exposed for approximately 1 day.

3. Chemical Exposure. The exposure protocol involves placing the required number of specimens (four for specific gravity) for each plastic material in containers (cells) containing the waste type and exposing them to the wastes or 14 days at 60°C. Different specimens of materials may be exposed at the same time in the exposure cell provided that sufficient waste is present for the total exposed surface area. For relatively insoluble materials, ASTM D543[7] recommends about 10 mL/in^2 (~1.6 mL/cm^2). For elastomeric materials, the test method recommends about 40 mL/in^2 (~6.2 mL/cm^2). Where elevated temperatures are used, it is important that the simulant waste be at the elevated test temperature before the specimens are placed in the test liquid. The exposure cells will be stirred every 24 hrs. by moderate magnetic stirring or other suitable means such as gentle swirling.

B. Comprehensive Evaluations

Those materials passing the screening tests are evaluated under four different radiation doses, four temperatures, and four exposure times in the four waste forms described above. The radiation levels chosen are 143,000, 286,000, 571,000, and 3,672,000 rads of γ-radiation from a ^{60}Co source. The exposure temperatures selected are 18, 23, 50, 60°C. Exposure times of 7, 14, 28, and 180 days are used. In addition to the specific gravity and permeability testing, the response of these materials are further evaluated based on their dimensional changes (ASTM D471), hardness changes (ASTM D2240), tensile property changes (ASTM D412, D638, and D945), stress cracking (ASTM D1693), and compression set changes (ASTM D395).

III. DISCUSSIONS

The purpose of a Chemical Compatibility Program is to provide a scientifically defensible methodology for measuring the chemical compatibility of polymeric liner and seal materials with hazardous wastes. These polymeric materials are those which may be used in current and future container designs for the transportation of hazardous and mixed wastes throughout the DOE complex. The approach for developing such a program was to assess the current state of chemical compatibility testing technology and direct the thinking of all those concerned toward routes that might lead to satisfactory, comprehensive, and reliable chemical compatibility data for use by the U. S. DOE in its Transportation Management Division.

Based on a review of the large body of chemical compatibility information, it is important to be aware of the basic factors that play a role in determining chemical compatibility of polymers (plastics) with various chemical environments. Polymer-environment interactions can be either reversible (absorption leading to plasticization and swelling) or irreversible (oxidation). These may also be referred to as physical (reversible) and chemical (irreversible) interactions although the physical interactions have a significant chemical aspect in the breaking of secondary interchain bonds. In general, polymers are resistant to weak acids, weak bases, and salt solutions. Strong acids can oxidize polymers leading to embrittlement. Organic solvents cause swelling, softening, and eventually dissolution. Most chemical degradation is system-specific for a particular polymer and fluid or gas. It is unlikely, therefore, that the kind of chemical compatibility information between polymers and any complex waste form being required for regulatory assurance will be found in the literature. For this reason, liner and seal materials selected in the design of transportation packagings will require compatibility testing with simulated wastes to ascertain their chemical resistance to these substances.

The container liner provides a barrier between the waste material(s) and the container structure. The liner itself is not expected to see significant structural loads in service. Emphasis for liner material selection is on chemical compatibility. Liner material properties potentially most affected by chemical exposure are dimensional stability, permeability, and hardness. Stress cracking in the presence of some chemicals may also occur. Seals found in many packages are devices or systems that create a tight union between elements of the container. These devices consist of a polymer that can be or has been modified to a state exhibiting little plastic flow and quick or nearly complete recovery from an extending force. Polymers of this type are also referred to as elastomers.

The main threats to seals and liners from the anticipated waste forms are judged to come from strong aqueous base, chlorinated solvents, hydrocarbon solvents, and ketones. Because few polymers are resistant to all these materials, it is possible that different polymers will be chosen as container components for the different waste streams being transported. The candidate liner and seal materials which are known to be chemically resistant to the above described waste forms, are butadiene-acrylonitrile copolymer, cross-linked polyethylene, epichlorhydrin, ethylene-propylene rubber, fluorocarbon, glass-filled tetrafluoroethylene, high-density polyethylene, isobutylene-isoprene copolymer, polypropylene, and styrene-butadiene rubber.

Because of the wide variety of waste compositions found throughout the DOE complex, it is not possible to choose on one specific simulant waste composition. In addition, since no specific transportation container has been selected or has been specified for certain waste compositions, it is not possible nor prudent to select a very specific waste composition. However, there is sufficient information in the open literature and in DOE reports that provides some guidance on the quantities and character of the larger waste streams found within the DOE complex. Based on this rationale, four simulant mixed waste compositions were selected. To simulate some of the tank wastes at the Hanford Site, a rather simple aqueous solution of 2 molar sodium nitrate, 0.7 molar sodium nitrite, 2 molar sodium hydroxide, 5.5 molar sodium carbonate, containing 0.1 molar cesium chloride and 0.1 molar strontium chloride. The nitrate/nitrite combination represent oxidizing chemical species while the hydroxide and carbonate simulate the corrosive nature of the tank wastes. The last two constituents simulate the radioactive component in this large volume waste stream. To simulate the sizable inventories of chlorinated hydrocarbons mixed wastes, a solution of 50% by volume of trichloroethylene, 25 % chlorobenzene, 24% carbon tetrachloride and 1% cerium (III) 2-ethyl hexanoate was selected. This mixture of chemicals is believed to qualitatively represent the chlorinated solvent waste streams at the DOE sites. The cerium salt simulates uranium and other actinide elements because of similarities in ionic radii and redox properties.. Similarly, to simulate liquid scintillation fluids and/or fuel hydrocarbons, a solution of 33% toluene, 33% xylene, 32% dioxane with 1% water will be used. The water component is meant to simulate tritiated water found in some mixed wastes. Finally, to simulate ketones, a solution of 60% MEK and 39% MIK containing 1% cerium (III) acetyl acetonate hydrate will be used. It should be mentioned that ketones were solvents frequently used in the nuclear fuel reprocessing cycle.

The variables in chemical compatibility testing represent those factors that are meant to simulate the conditions under which the material being evaluated will be used under normal and, in some cases, under abnormal conditions. Specifically, the more important of these variables include exposure temperature, exposure time, radiation dose, and waste liquid concentration.

Some standard testing methods specify exposure temperatures of 23°C and 50°C. Since the purpose of this program is to evaluate the effects of hazardous materials on transportation container components, it is worthwhile to mention that the Department of Transportation (DOT) regulations in 49 CFR 173.24 (e)(3)(ii) require chemical compatibility testing at temperatures of 18, 50, and 60°C. In this program, we have therefore chosen a combination of these temperatures, i.e., 18, 23, 50, and 60°C.

As with exposure temperatures, in standardized testing methods, the duration of exposure varies with each test protocol. However, regardless of the actual test duration, most groups involved in chemical compatibility testing agree that what is required is a three-level approach involving short-duration, intermediate, and long-duration exposure. The short duration tests are considered a good way to screen materials for further testing. Intermediate duration are considered to be 4 months in length. Long duration tests are considered by some to be more than 4 months in length. DOT specifies such a testing duration scheme for its plastic packaging used for liquid hazardous materials. Accordingly, we have selected exposure times of 7, 14, 28, and 180 days to include short and long duration times.

With regard to radiation dose, some international standards recommend that materials be exposed to absorbed doses ranging from 10^5 to 10^{10} rads. While the doses recommended by these standard, span a range where no effects in material properties are expected to where plastic materials are expected to be severely damaged, the transportation containers for mixed wastes are not expected to receive doses above 10^4 rads. We have selected γ-radiation doses of 143,000, 286,000, 571,000, and 3,672,000 rads from a ^{60}Co source. These radiation values were calculated based on γ-ray dose rate data available to us that the components of a pump submerged in a specific storage tank at Westinghouse Hanford Co. are calculated to be expected to receive. These data indicate a maximum γ-ray dose rate in the range of 750 to 850 R/hr. The maximum dose rate of 850 rad/hr was used in calculating the dose that container materials will receive from a ^{60}Co source at SNL. Using this dose rate, the four doses described above were calculated for 7, 14, 28, 180 day exposures, respectively.

A final variable for chemical compatibility testing is waste concentration. Practitioners of chemical compatibility evaluations generally believe that liner and seal materials should be tested with the actual concentration of waste. Exposure to pure chemicals is generally rejected since it does not simulate actual conditions where concentrations are usually lower. This especially true where complex mixtures of many chemical are concerned. A generally accepted concentration is exposure to 10 times the expected actual concentration. This value was considered a good way to simulate a worst-case situation. For transportation containers, such a worst-case could involve the evaporation, i.e., leakage from a container, of the contained waste.

A variety of properties have been proposed and used for evaluating liner and seal materials. Of primary interest to most organizations is resistance to chemicals in wastes. For organizations concerned with mixed waste forms, the materials resistance to both chemicals and radiation are of interest. Depending on the levels of radiation in the mixed waste, i.e., where low-levels of radiation are expected, resistance to chemicals may be of greater interest. Chemical compatibility is usually based on static physical test data gathered after exposure of the material to a chemical (leachate, surrogate, or simulant). By far the simplest of such testing involves changes in mass and dimensions. Since specific gravity measurements combine these two units in one method, this method is particularly attractive for screening tests. Physical test data may also include tensile properties such as tensile strength, yield strength, elongation at break, elongation at yield, and some others. These one-dimensional, short-term, simple tests are easily accomplished in the laboratory. Additional physical tests may include tear and puncture resistance of the plastics and hardness. However, since liners and seals in packaging applications are not expected to be exposed to such failure modes, the latter tests will be omitted.

Traditionally, in plastics and rubber testing, the static physical tests led by hardness and tensile stress/strain measurement are used to indicate changes and degradation. The stress/strain properties are related to the molecular makeup of the polymer, so that any attack or alteration in the polymer structure configuration is manifested by stress/strain changes. Most of these physical tests, whether in tension, compression, shear, or bending (a combination of all three modes) specified for polymers, have been adapted from traditional methods for metals. In polymer technology, it is assumed that a simple, single test of short-term mechanical nature at an arbitrary combination of time and temperature and in one physical state is useful for evaluating the general performance of plastic materials. A special consideration is the fact that in physical testing the value and meaning of observed changes are not always clear. Is no change in value necessary for compatibility, or is 5%, 10%, etc., adequate?

The proposed testing strategy shown in Figure 1 uses a screening technique to limit the number of materials being subjected to more comprehensive testing. In this strategy, screening criteria values of 10% for specific gravity and 0.9 g/m^2/h for permeability rates were selected. These values were chosen because they have been cited in the literature[8] as qualitative criteria in determining the chemical resistance of materials used in liner applications. As shown in Figure 1, those materials which exhibit lower values are determined to pass the screening test while those with higher values fail the tests. These latter materials would be eliminated from further testing. All testing data

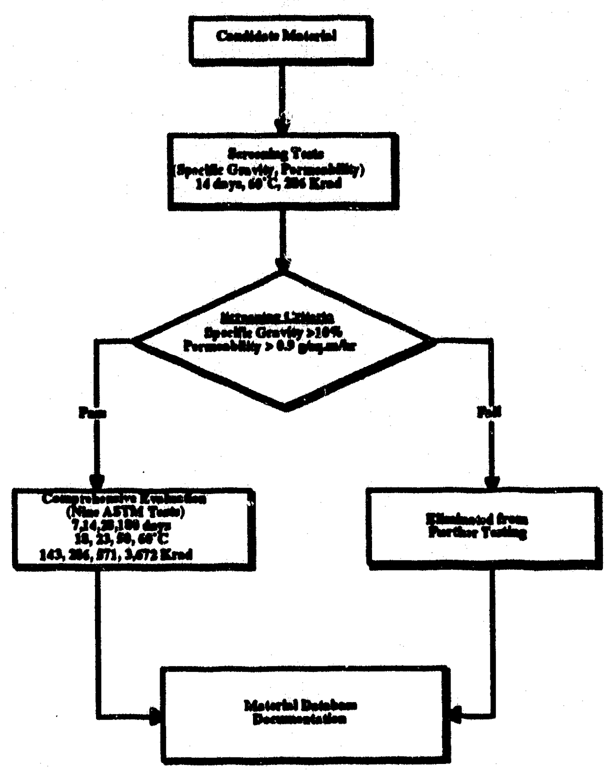

Fig. 1 Chemical Compatibility Testing Strategy

would be compiled in a material database which would be available to packaging designers or additional parties within and external to the DOE. The selection of specific gravity and permeability as screening tools is based on the availability of national standards, i.e., ASTM D792 and ASTM D814, that describe the use of these properties to test plastics. In addition to being easily performed with inexpensive laboratory equipment, these tests provide data on materials consistent with their intended application. For example, where a material exhibits changes in specific gravity, i.e.,. changes its density, the materials may be losing some of the specific desirable properties for which they were selected. Such properties might be flexibility, radiation resistance, and chemical resistance. The use of permeability in evaluating materials for sealing applications is certainly obvious. What may not be as obvious is the numerical value for permeability rates of 0.9 $g/m^2/hr$. While this value may be valid for flexible liners used in hazardous waste landfill applications[8], its application to packaging components may be tenuous. However, the fact that permeability rates are used in packaging regulations, i.e., by the DOT in Appendix B of 49 CFR 173, there appears to be some validation for its use.

Finally, while no further criteria have been proposed for those materials which are subjected to the comprehensive evaluations shown in Figure 1 and described in Section II. B, it should be mentioned that this testing program could "down-select" materials further based on the additional criteria reported by Schwope, et al[8].

IV. CONCLUSIONS

We have described a Chemical Compatibility Program for the evaluation of transportation packaging components which may be used in transporting mixed waste forms. This testing program uses γ-radiation doses of 143,000, 286,000, 571,000, and 3,672,000 rads, exposure times of 7, 14, 28, and 180 days, exposure temperatures of 18, 23, 50, 60°C with four simulant waste forms. These simulant wastes are (1) an aqueous alkaline mixture of sodium nitrate and sodium nitrite; (2) a chlorinated hydrocarbon mixture; (3) a simulant liquid scintillation fluid; and (4) a mixture of ketones. A selection of 10 polymers with anticipated high resistance to one or more of these types of environments have been proposed for testing as potential liner or seal materials.

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