NISTIR 4346

DEVELOPMENT OF TEST METHODS TO DETERMINE THE COMPATIBILITY OF LIQUID HAZARDOUS MATERIALS WITH POLYETHYLENE PACKAGINGS

J. M. Crissman

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards
and Technology
Materials Science and Engineering
Laboratory
Polymers Division
Gaithersburg, MD 20899

Prepared for
U.S. Department of Transportation
Research and Special Programs
Administration
Office of Hazardous Materials
Transportation

U.S. DEPARTMENT OF COMMERCE
Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Dr. John W. Lyons, Director

NIST

NISTIR 4346

DEVELOPMENT OF TEST METHODS TO DETERMINE THE COMPATIBILITY OF LIQUID HAZARDOUS MATERIALS WITH POLYETHYLENE PACKAGINGS

J. M. Crissman

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards
and Technology
Materials Science and Engineering
Laboratory
Polymers Division
Gaithersburg, MD 20899

Prepared for
U.S. Department of Transportation
Research and Special Programs
Administration
Office of Hazardous Materials
Transportation

May 1990

U.S. DEPARTMENT OF COMMERCE
Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Dr. John W. Lyons, Director

ABSTRACT

This report describes work done for the Department of Transportation, Office of Hazardous Materials Transportation to develop test methods which can be used to determine whether a liquid hazardous material may be shipped in a specific type of polyethylene packaging. Current federal regulations require that each prospective lading be tested individually in proposed polyethylene packagings and do not make provision for liquids which may be unstable at 21°C. One area being explored is the possibility of dividing the liquids into groups and authorizing the transportation of all the liquids in the group based on tests done using one standard liquid from that group. The feasibility of basing compatibility tests on the use of standard liquids is assessed and recommendations are made as to the conditions under which such a scheme can be used. An empirical scheme known as the "Permachor" method for ranking the permeability of liquid hazardous materials is proposed.

Key Words: Compatibility; hazardous materials; organic peroxides; permachor; permeation; polyethylene; standard liquid.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

DEVELOPMENT OF TEST METHODS TO DETERMINE THE COMPATIBILITY OF LIQUID HAZARDOUS MATERIALS WITH POLYETHYLENE PACKAGINGS

(1) INTRODUCTION

This report describes work done under reimbursable agreement DTRS-57-89-X-00121 for the Department of Transportation, Office of Hazardous Materials Transportation (OHMT). The objective of this project is to develop practical and cost-effective test methods which can be used to determine whether a liquid hazardous material may be shipped in a specific type of polyethylene packaging. Current federal regulations (Title 49, Section 173.24 (d)) require that each individual liquid be tested in the proposed polyethylene packaging and do not make any provision for testing liquids which may be unstable at 21°C(70°F). The OHMT wishes to explore the possibility of dividing the liquids into groups and authorizing the transportation of all the liquids in a group based on tests using one standard liquid from that group. (This procedure is currently allowed under European regulations.) The OHMT is also interested in developing test methods suitable for evaluating the compatibility of polyethylene with materials unstable at 21°C(70°F) such as organic peroxides. It is anticipated that the results obtained from this project will enable the OHMT to amend Title 49 CFR so that assessment of chemical compatibility of polyethylene packagings can be improved.

The National Institute of Standards and Technology has been requested to address the following tasks:

Task 1. Develop a test program to evaluate the compatibility of liquid hazardous materials with polyethylene packagings based on generic groupings of materials.

The following subtasks are to be addressed:

(A) Review current DOT test requirements to see if they can be modified to accomplish Task 1;

(B) Review the European (ADR/RID) approach to testing and compare their methods with current DOT methods; and

(C) Recommend testing procedures based on grouping of hazardous liquids which can be used as a basis for rulemaking.

Task 2. Develop a compatibility test procedure for liquids such as organic peroxides that are unstable at 21°C(70°F).

The following subtasks are to be addressed.

(A) Contact the manufacturers of organic peroxides to determine how they are testing for compatibility with polyethylene the peroxides that are unstable at 21°C;

(B) Review the literature to ascertain the current state of knowledge concerning the compatibility of organic peroxides with polyethylene packagings;

(C) Develop guidelines which might be used to predict the compatibility of organic peroxides with polyethylene packagings; and

(D) Evaluate the possibility of using materials other than organic peroxides to predict the compatibility of organic peroxides with polyethylene packagings.

(2) REVIEW OF CURRENT DOT REGULATIONS (TITLE 49 CFR) [1][1]

A summary of current DOT regulations as they pertain to the transportation of liquid hazardous materials in polyethylene packagings is given in Table 1. It can be noted that in earlier editions of Title 49 CFR (for example the 1974 edition) under paragraph 178.24 there were four material specification requirements: (1) melt index $\leq$ 2.6; (2) density in the range from 0.910 - 0.925 g/cm^3; (3) tensile strength a minimum of 1500 pounds per square inch (psi); and tensile elongation a minimum of 400 percent. Under paragraph 173.24(d) "Standard requirements for all polyethylene packagings", the current regulations contain no materials specifications. The current regulations represent a performance oriented approach.

With regard to compatibility, current DOT regulations require that tests be carried out with each type or combination of hazardous material. There is a maximum loss requirement of $\leq$ 0.5 per cent for materials meeting the definition of a poison and $\leq$ 2 per cent for other hazardous materials.

(3) REVIEW OF CURRENT EUROPEAN REGULATIONS (ADR APPENDIX A.5) [2]

A summary of the current European regulations as they pertain to the transportation of hazardous materials in polyethylene packagings is presented in Table 2. The European test requirements for plastic packagings are shown in Table 3 and a list of the standard liquids for verifying chemical compatibility as well as a representative list of substances for which the standard liquid may be regarded as equivalent are given in Tables 4 and 5. European regulations place two specifications on the material to be used: The melt flow rate must be $\leq$ 12 g/10 min under condition 190°C/21.6 kg load and the density after thermal treatment at 100°C for one hour must be $\geq$ 0.940 g/cm^3. Under marginal (3551)(2) the maximum allowable permeation rate is 0.008 g/hr at 23°C. Under marginal (3553)(5) in the leakproofness test an air pressure of not less than 20 kPa(2.9 psi) is specified, however no duration of the test is specified.

---

[1] Numbers in brackets identify references found at the end of this report.

TABLE 1

CURRENT DOT REGULATIONS

TITLE 49 CFR

(173.24d) Standard Requirements For All Polyethylene Packagings

(1) Materials specifications- none

(2) Compatibility- The maximum rate of permeation of lading to be shipped through or into the container shall not, under any of the following three test conditions, exceed 0.5 percent for materials meeting the definition of a poison and 2.0 percent for other hazardous materials. A minimum of three containers shall be tested for each combination of hazardous material and size and design of container.

(a) 180 days at a temperature no lower than 18°C(64°F)
(b) 28 days at a temperature no lower than 50°C(122°F)
(c) 14 days at a temperature no lower than 60°C(140°F)

(3) Other tests- To be carried out after the compatibility test. The container shall be drained, rinsed, and filled to capacity with water. At ambient temperature the container shall be dropped from a height of 1.2 meters (3.94 feet) onto solid concrete.

(178.16) Specification 35; Non-Reusable Molded Polyethylene Drum; Removable Head Required.

(1) Materials specifications-

(a) Drums shall be made of an injection molding grade of high density polyethylene resin which has not been used previously (density not specified). Regrind from the same production process may be used.
(b) Ultraviolet light protection may be provided by the addition of carbon black or other equally efficient pigment.

(2) Capacity- Rated capacity is not to exceed 26.5 liters (7 gallons).

(3) Qualification Tests- at the start of production on each drum size.

(a) Drop test- Similar in nature to that under 173.24d(3) except that the drums and their contents must be conditioned and tested at a temperature of -18°C(0°F) or lower.

(b) Vibration test- Three fully loaded test drums of each size and type must be placed on a platform that has a vertical double-amplitude (peak-to-peak displacement) of 2.54 cm (one inch). The test shall be performed for

one hour at a frequency that causes the drum to be raised from the platform to such a degree that a piece of material of approximately 0.16 cm (1/16 inch) thickness can be passed between the bottom of the drum and the platform.

(c) Static compression test- Two filled drums must be conditioned so that the drums and their contents are are at a temperature of 54°C(130°F) or higher at the start of each compression test. The two drums of identical capacity, stacked two high, must withstand a static compression test applied evenly for 48 hours to the top rim of the drum without buckling of the side walls or leakage. The compression weight load to be applied must be the greater of 136.4 kg (300 pounds) or the volume in gallons of one drum times 38.6 kg (85 pounds). Total top to bottom deflection of both drums may not exceed one inch.

(178.19) Specification 34; Reusable Polyethylene Drum For Use Without Overpack. Removable Head Not Authorized.

(1) Materials specifications-

(a) Drums shall be made of polyethylene resin which has not been used previously. Regrind from the same production process may be used.

(b) Ultraviolet light protection may be provided by the addition of carbon black or other equally efficient pigments provided they are compatible with lading and retain their effectiveness for the life of the drum.

(c) Other materials may be added provided they do not adversely affect the structural integrity of the drum.

(2) Capacity- Rated capacity not to exceed 208 liters (55 gallons).

(3) Qualification tests-

(a) To be performed at the start of production and at 4-month intervals. At least three filled containers shall be capable of withstanding the follow tests.

(1) Drop test- at least three containers.

(i) The container filled to 98% capacity with water shall be dropped from a height of 1.22 m (4 feet) onto solid concrete so as to drop diagonally on the top edge or any part constructed to a lesser strength (ambient temperature).

(ii) The container filled to 98% capacity with a solution compatible with polyethylene and which remains liquid at -18°C (0°F) shall be dropped from a

height of 1.22 meters (4 feet) onto solid concrete on any part of the container when container and contents are at or slightly below -18°C(0°F).

(2) Hydrostatic pressure test- The container shall be tested by retaining for 5 minutes hydrostatic pressure of at least 0.10 MPa (15 psi) at equilibrium without showing a pressure drop or evidence of leaking.

(b) At least three containers taken at random from each continuous production lot of no more than 1000 containers of each given type and size shall withstand without leakage or failure the test described above in 178.19(3)(a)(1).

(c) At least three containers of each size and type taken at random at the start of initial production, and upon any change of materials, design, or process method shall withstand without failure or leakage the following tests. No single container shall be expected to withstand more than one test.

(1) The container filled to 98% of capacity with water shall be capable of withstanding the vibration test described above under 178.16(3)(b).

(2) The container filled to 98% of capacity with water shall be capable of withstanding the following static compression test without buckling of the side walls sufficient to cause damage, but in no case shall the maximum top to bottom deflection be more than one inch. Compression shall be applied to the load bearing areas of the top of the container for a period of not less than 48 hours.

Rated capacity in liters (gallons)	Compression weight load in kg (pounds)
9.5 - 24.6 (2 1/2 - 6 1/2)	273 (600)
57 (15)	545 (1,200)
114 (30)	818 (1,800)
208 (55)	1091 (2,400)

CURRENT EUROPEAN REGULATIONS PERTAINING TO THE TRANSPORTATION OF HAZARDOUS MATERIALS IN POLYETHYLENE CONTAINERS
APPENDIX A.5

(3526) Plastic Drums And Jerricans

(1) General specifications-

(a) Ultraviolet light protection- Protection against ultraviolet light may be provided by the addition of carbon black or other suitable pigments or inhibitors.

(b) Period of use- The maximum permitted period of use of packagings for the transportation of hazardous materials shall be five years from the date of their manufacture.

(c) Capacity- Maximum capacity of drums: 450 liters (≃125 gallons)
Maximum capacity of jerricans: 60 liters (≃ 15 gallons)

(d) Net mass- Maximum net mass for drums: 400 kg (880 pounds)
Maximum net mass for jerricans: 120 kg (264 pounds)

(2) Permeation- The maximum permissible permeation rate for inflammable liquids at 23°C (73°F) shall be 0.008 g/hr. (This value is apparently independent of the container size.)

3551 Preparation Of Packagings And Packages For Testing-

(1) Packagings for liquids shall be filled to not less than 98% of their capacity. The substances to be carried in the packages may be replaced by others except where this would invalidate the results of the tests.

(2) In the drop tests for liquids, when another substance is used its relative density and viscosity shall be similar to those of the substance to be carried.

(5) To check that their chemical compatibility with the liquids is sufficient, plastic drums and jerricans, in accordance with marginal 3526 shall be subjected to storage at ambient temperature for six months, during which time the test samples shall be kept filled with the goods they are intended to carry. For the first and last 24 hours of storage the test samples shall be placed with the closure downward.

(3551 Cont'd)

(6) High molecular mass polyethylene drums and jerricans in accordance with marginal 3526 must conform to the following specifications:

(a) Density- The relative density at 23°C (73°F), after thermal conditioning for one hour at 100°C (212°F), must be ≥ 0.940 g/cm^3 in accordance with ISO Standard 1183.

(b) Melt flow rate- The melt flow rate under condition 190°C/21.6 kg load must be ≤ 12 g/10 minutes in accordance with ISO Standard 1133.

(c) Compatibility- The chemical compatibility of the packaging with the lading shall be verified by storage for three weeks at 40°C (104°F) using one of the standard liquids listed in Table 4. Where the standard liquid is water, proof of chemical compatibility is not required. For the first and last 24 hours of storage, the test samples shall be placed with the closure downwards.

TABLE 3

EUROPEAN TEST REQUIREMENTS FOR PLASTIC PACKAGINGS FOR HAZARDOUS MATERIALS

(3552) Drop Test-

(1) Number of samples- Six samples (three for each drop)
(a) First drop- The packaging shall strike the target diagonally on the chime or, if the packaging has no chime, on a circumferential seam or an edge.
(b) second drop- The packaging shall strike the target on the weakest part not tested by the first drop.

(2) Temperature- Testing of plastic drums shall be carried out when the temperature of the test sample and its contents has been reduced to -18°C(0°F) or lower.

(3) Test liquid- The test liquid shall be kept in a liquid state, if necessary by the addition of anti-freeze.

(4) Drop height- For aqueous solutions of hydrogen peroxide a drop height of from 0.8 to 1.2 meters (2.63 - 3.94 feet) shall be used. The standard liquid for aqueous solutions of hydrogen peroxide is water.

(5) Criteria for passing the test- Every package containing liquid shall be leakproof when equilibrium has been reached between the internal and external pressures.

(3553) Leakproofness Test-

(1) Packaging type- The leakproofness test shall be performed on all types of packagings intended to contain liquids.

(2) Number of test samples- Three test samples per design type and manufacturer shall be tested.

(3) Test sample preparation- Test samples shall be pierced for entry of the compressed air at a neutral point, so as also to test the tightness of the closure.

(4) Test method- The test samples shall be immersed in water; and shall be kept under water in such a way as not to distort the result of the test. The packaging may also be covered with soap solution, heavy oil or other suitable liquid on the seams or at any other place where leakage might occur. Other equally effective methods may also be used.

(5) Air pressure to be applied- For solutions of organic peroxides not less than 20 kPa (2.9 psi).

(6) Criterion for passing the test- There shall be no leakage.

(3554) Internal Pressure (Hydraulic) Test-

(1) Packaging type- The hydraulic pressure test shall be carried out on all types of polyethylene drums and jerricans intended to contain liquids.

(2) Number of test samples- Three test samples per design type and manufacturer.

(3) Test preparation- Test samples shall be pierced for entry of the pressure at a neutral point, so as also to test the tightness of the closure.

(4) The packagings shall be subjected for 30 minutes to a hydraulic gauge pressure not lower than:

(a) the total gauge pressure measured in the packaging (i.e. the vapor pressure of the filling substance and the partial pressure of the air or other inert gas, less 100 kPa (14.5 psi)) at 55°C(131°F), multiplied by a safety factor of 1.5, or

(b) 1.75 times the vapor pressure of the filling substance at 50°C(122°F), less 100 kPa (14.5 psi), but at a gauge pressure of not less than 100 kPa, or

(c) 1.5 times the vapor pressure of the filling substance at 55°C(131°F), less 100 kPa (14.5 psi), but at a gauge pressure of not less than 100 kPa.

The manner in which the packagings are maintained in place shall not distort the results of the test. Pressure shall be applied continuously and evenly. The test pressure shall be kept constant throughout the test period.

(3555) Stacking Test-

(1) Packaging type- All polyethylene drums and jerricans shall be subjected to the stacking test.

(2) Number of test samples- Three test samples per design and manufacturer.

(3555) CONT'D

(3) Test method- The test samples shall be capable of withstanding an additional mass placed on a flat surface resting on the test sample and equivalent to the total mass of identical packages which might be stacked on it during carriage.

(a) For plastic drums and jerricans intended for the carriage of liquid the duration of the test shall be 28 days at 40°C(104°F).

(b) The stacking height to be allowed for shall be at least 3 m.

(c) In the stacking test account shall be taken of the highest relative density of filling substance to be approved.

(d) For the test in accordance with marginal 3551 (6), a stacking test shall also be carried out with a standard liquid. The mass of the stacking load shall be determined on the basis of the highest relative density of filling substance to be approved.

(4) Criteria for passing the test-

(a) No test sample shall leak.

(b) No test sample shall show any deterioration or distortion which could adversely affect transport safety or is liable to reduce its strength or cause instability in stacks of packagings.

(3556) Supplementary Permeability Test For Plastic Drums And Jerricans In Accordance With Marginal (3526)

(1) Package type- Polyethylene packagings need be subjected to this test only if they are to be approved for the carriage of benzene, toluene, or mixtures and preparations containing those substances.

(2) Number of test samples- Three packages

(3) Test sample preparation- The test samples are to be pre-stored with the original filling substance in accordance with marginal 3551 (5). For high molecular mass polyethylene packagings, the standard liquid shall be a mixture of hydrocarbons (white Spirit) in accordance with marginal 3551 (6).

TABLE 3 (CONT'D)

(4) The test samples filled with the test substance for which the package is to be approved shall be weighed before and after storage for 28 days at 23°(73°F) and 50 percent relative humidity. For high molecular mass polyethylene packagings, the test may be carried out with the standard liquid mixture of hydrocarbons (white spirit) in place of benzene, toluene, or xylene.

(5) Criterion for passing the test- The permeation rate shall not exceed 0.008 grams per hour.

TABLE 4

Standard Liquids For Verifying Chemical Compatibility Of High Molecular Mass Polyethylene Packagings (Annex To Appendix A.5)

(1) Wetting Solution- for substances causing severe cracking in polyethylene under stress, in particular for all solutions and preparations containing wetting agents. An aqueous solution of 1 - 10 percent of a wetting agent shall be used. The surface tension of this solution shall be 31 to 35 mN/m at 23°C (73°F).

The stacking test shall be carried out on the basis of a relative density of not less than 1.20 g/cm^3.

(2) Acetic Acid- for substances and preparations causing cracking in polyethylene under stress, in particular for monocarboxylic acids and monovalent alcohols. Acetic acid in 98 - 100 percent concentration shall be used.

The stacking test shall be carried out on the basis of a relative density of not less than 1.05 g/cm^3.

A compatibility test with acetic is not required if adequate chemical compatibility is proved with a wetting solution.

(3) Normal Butyl Acetate/Normal Butyl Acetate-Saturated Wetting Solution- for substances and preparations causing polyethylene to swell to such an extent that the polyethylene mass is increased by up to about 4 percent and at the same time causing cracking under stress, in particular for phyto-sanitary products, liquid paints and esters. Normal butyl acetate in 98 - 100 percent concentration shall be used for preliminary storage in accordance with 3551(5).

The stacking test shall be carried out on the basis of a relative density not less than 1.0 g/cm^3.

(4) Mixture of Hydrocarbons (White Spirit)- for substances and preparations causing polyethylene to swell to such an extent that the polyethylene mass is increased by less than 7.5 percent, in particular for hydrocarbons, esters and ketones. A mixture of hydrocarbons having a boiling zone of 180 - 200°C (356 - 414°F), a relative density of 0.79 g/cm^3, a flash point above 61°C (142°F) and an aromatic content 16 - 18 percent (C_9 and higher aromatics only) shall be used.

The stacking test shall be carried out on the basis of a relative density not less than 1.0 g/cm^3.

TABLE 4 (CONT'D)

In the case of filling substances causing polyethylene to swell to such an extent that the polyethylene mass is increased by more than 7.5 percent, adequate chemical compatibility may be proved after preliminary storage for three weeks at 40°C (104°F), in accordance with marginal 3551(5) specified above but with the original filling matter.

(5) Nitric Acid- for all substances and preparations having an oxidizing effect on polyethylene and causing molecular degradation identical to or less than 55 percent nitric acid. Nitric acid in 55 percent concentration shall be used.

The stacking test shall be carried out on the basis of a relative density of not less than 1.4 g/cm^3.

(6) Water- for substances which do not attack polyethylene in any of the cases referred to under (i) to (v), in particular for inorganic acids other than nitric acid, lyes, aqueous saline solutions, polyvalent alcohols and organic substances in aqueous solution.

The stacking test shall be carried out on the basis of a relative density of not less than 1.2 g/cm^3.

TABLE 5

REPRESENTATIVE LIST OF SUBSTANCES TO WHICH THE STANDARD LIQUIDS MAY BE REGARDED AS EQUIVALENTS IN ACCORDANCE WITH MARGINAL 3551(5) IN TABLE 2

SUBSTANCE	STANDARD LIQUID
Crude petroleums and other crude oils	Mixture of hydrocarbons
Hydrocarbons	"
Halogenated substances	"
Ethers	"
Aldehydes	"
Ketones	"
Petroleum, solvent naptha	"
White spirit	"
Nitrogenous substances	"
Heating oils, diesel oils	"
Oxygenated substances	"
Waste sulphuric acid	"
Ammonia solutions	"
Alcohols	Acetic acid
Aniline	"
Phenol	"
Ethylene glycol mono-butyl ether	"
Furfuryl acid	"

TABLE 5 (CONT'D)

SUBSTANCE	STANDARD LIQUID
Cresols	Acetic acid
Alkyl phenols	"
Acrylic acid, formic acid	"
Thioglycolic acid	"
Methacrylic acid	"
Propionic acid	"
Esters	Normal butyl acetate
Nitric acid	Nitric acid
Aqueous solutions of perchloric acid	"
Chromic acid	"
Hypochlorite solutions	"
Solutions of hydrochloric, hydrobromic, hydriodic, hydrofluoric, fluoboric and fluosilicic acids	Water
Phosphoric acid	"
Sulphuric acid	"
Soda lye, potash lye and caustic lye	"
Aqueous solutions containing formaldehyde	"
Aqueous solutions containing hydrogen peroxide	"

(4) COMPARISON OF CURRENT DOT AND EUROPEAN REGULATIONS

While in many respects the two sets of regulations are similar, there are some significant differences which should be singled out. As noted above, DOT regulations, as they pertain to polyethylene packagings, are solely performance oriented, whereas the European regulations contain two materials specifications as well as the performance evaluations. In the case of an all plastic packaging, the density requirement (≥ 0.940 g/cm^3 after a one hour heat treatment at 100°C) is, presumably, intended to minimize permeation and at the same time satisfy the ADR test requirements of the static compression or stacking test. A melt flow rate (MFR) of less than 12 g/10 min places some restriction on the minimum molecular weight of the polyethylene resin, there being an inverse relationship between the molecular weight and MFR. Molecular characteristics such as molecular weight and degree or type of branching are also important factors in determining stress-crack resistance in polyethylene. A higher molecular weight generally leads to improved stress-crack resistance.

There are also several similarities and differences among the various test methods between the two sets of regulations.

(A) Compatibiity Testing - The two major differences are:

(i) The maximum permeation rate allowed under DOT regulations is 0.5 per cent for materials meeting the definition of a poison and 2.0 per cent for other hazardous materials. For a 208 liter (55 gallon) container this translates into a loss at the end of the test period of about 0.275 gallons for a poison and 1.1 gallons for other hazardous materials. On the other hand the European regulations stipulate that the loss can be no more than 0.008 grams/hour at 23°C over the course of the test. This amount appears to have been chosen independent of the size of the container or area in contact with the permeant. This means that after the 28 day test period the maximum amount of material lost from the same 208 liter container must be no more than approximately 4 grams (≈4 cubic centimeters).

(ii) Current DOT regulations require that polyethylene packagings must be tested with each type of lading to be shipped. European regulations, on the other hand, allow for the testing to be done using the six standard liquids list in Table 4. A representative list of substances for which the standard liquids may be regarded as equivalents is given in Table 5. It should be noted that the only peroxides listed in the Annex To Appendix A.5, Section II, ADR are aqueous solutions of hydrogen peroxide for which the standard test liquid is water.

(B) Drop test- This test is substantively the same in both sets of regulations.

(C) Hydrostatic pressure test-leakproofness test- While these two tests are similar in nature and require compressed air, there are three differences. Neither test specifies a temperature or temperature range in which the test is to be carried out.

(i) DOT regulations require a minimum internal pressure of 103 kPa

(i) DOT regulations require a minimum internal pressure of 103 kPa (15 psi), whereas the European regulations specify a minimum pressure of 30 kPa(4.37 psi).

(ii) The European test is to be done under water, whereas no test environment is specified in the DOT regulations.

(iii) The DOT test specifies a minimum time under the test pressure of 5 minutes, whereas no time under test is specified in the European requirements. This latter difference would appear to render the European test rather meaningless. This hydrostatic pressure test is seemingly intended to test principally the closure of the container because of its relatively short duration. This test will be most effective if the pressure is applied at a location other than through a closure.

(D) Hydraulic test- This test is not required by DOT.

(E) Vibration test- This test is not required in Europe.

(F) Static compression test-stacking test- Although these two tests are different in nature, they are both intended to test the packagings ability to withstand an additional mass likely to be encountered during shipping and storage. The European test involves the use of actual shipping containers filled with a standard liquid and held under test at 40°C(104°F) for 2 days with a minimum stacking height of 3 meters. DOT regulations, on the other hand, allow for the use of static dead load weights (specified according to the container volume) for a period of not less than 48 hours at an unspecified temperature. This test would be more meaningful if a minimum test temperature were specified.

(5) PHYSICAL TESTING OF POLYETHYLENE CONTAINERS

The need for testing of polyethylene based packagings arises from the observation that the mechanical integrity of polyethylene can be compromised in various ways by the presence of one or more of at least three different classes of chemical agents. This is demonstrated in Figure 1 [3] for polyethylene under a uniaxial stress in the presence of two types of chemical environments. Plotted along the ordinate is the logarithm of the time to failure in the presence of a chemical environment, and along the abscissa is the logarithm of the time to failure in air, for pairs of experiments done at the same level of applied stress. The dashed line represents the behavior to be expected if there were no decrease in lifetime as a result of the presence of the chemical

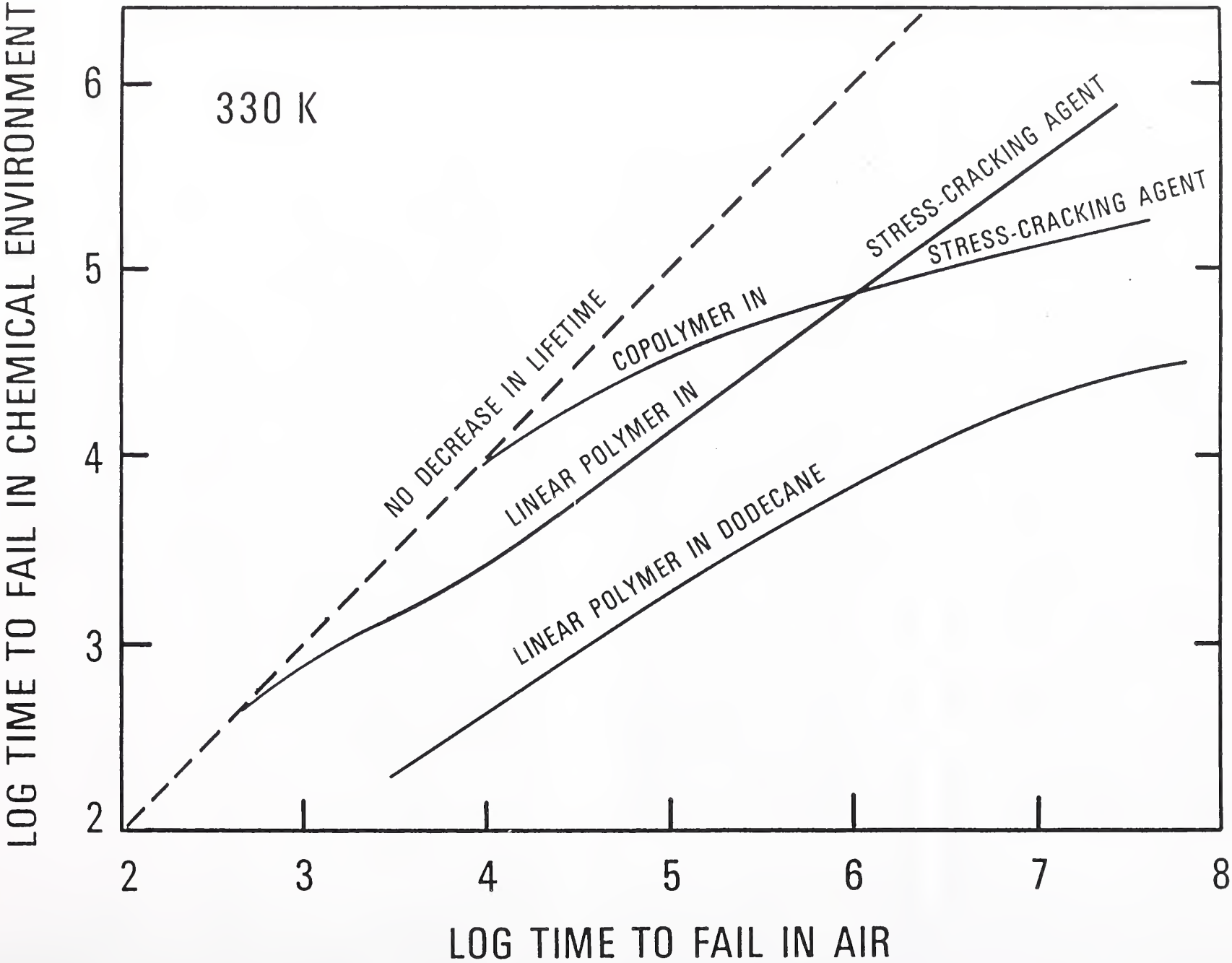

Figure 1. Log Time to Fail in Adverse Chemical Environment Versus Log Time to Fail in Air for High Density Polyethylene and an Ethylene-Hexene Copolymer. (Figure Reproduced from Reference [9].)

agent. In the presence of a stress-cracking agent, such as a detergent or wetting agent, polyethylene under stress will eventually form cracks which can lead to failure. This class of chemical agent does not necessarily permeate through the polyethylene and appear on the outside of a container unless a crack penetrates completely through a wall of the container. In the experiments summarized in Figure 1 the stress-cracking agent used was a 10 per cent solution of nonylphenoxy(polyethyleneoxy)ethanol in distilled water. It can be seen that, in the presence of the stress-cracking agent, when the experiment is done at relatively high stresses (short failure times) there is no decrease in lifetime relative to that in air. However as the applied stress is decreased there can be a significant decrease in failure time from that found in air, to the extent that the lifetime may be shorter by several decades in time.

A second class of chemical agent which can affect mechanical performance is one which actually permeates through the wall of the container and may be lost to the external environment. These agents, which include many organic solvents, are also swelling agents. An example of this type of behavior is indicated in Figure 1 by the line representing failure in dodecane ($C_{12}H_{26}$). The shortening of the failure time with respect to that in air is even more pronounced than in the case of the stress-cracking agent.

The third type of chemical compounds which may have a detrimental effect on the mechanical behavior polyethylene is a strong oxidizing agent such as nitric acid. Nitric acid at elevated temperatures is believed to preferentially attack the amorphous fraction of the polymer causing bond scission and degradation of the material. With regard to tests for compatibility it is important to recognize that all three classes of chemical compounds can contribute to the deterioration of mechanical performance and therefore need to be addressed in the testing procedures.

(6) INDUSTRY SURVEY OF ORGANIC PEROXIDES BEING SHIPPED IN POLYETHYLENE PACKAGINGS

Contact with a number of the major producers and shippers of organic peroxides indicate that there are a large number of organic peroxides being shipped using a variety of liquid diluents and shipping conditions. A partial listing of these materials is given in Table 6. Common diluents range from various phthalates to odorless mineral spirits (OMS) which may be comprised of a variety of liquid hydrocarbons including dodecane. In Table 6 it can be seen that OMS is the most commonly used diluent.

(7) PERMEATION OF ORGANIC LIQUIDS THROUGH POLYETHYLENE

There is, as yet, no theory which can be used to correlate the permeabilities of a large number of different ladings. There is, however, an

TABLE 6

PARTIAL LIST OF ORGANIC PEROXIDES SHIPPED IN POLYETHYLENE CONTAINERS

FAMILY NAME	PEROXIDE NAME	FORM	DILUENT	MAXIMUM STORAGE TEMPERATURE °C(°F)	SADT[1] °C(°F)
t-AMYL PEROXIDES	t-amyl peroxy-neodecano-ate	solution	OMS[2]	-10(14)	25(77)
	t-amyl peroxy-pivalate	solution	OMS	-7(20)	NA[3]
	t-amyl peroxy-2-ethyl-hexanoate	liquid	none	10(50)	45(113)
	t-amyl peroxy-acetate	solution	OMS	38(100)	NA
	1,1-di(t-amyl-peroxy)-cyclohexane	solution	BBP[4]	38(100)	80(176)
	OO-t-amyl O-(2-ethylhexyl)-monoperoxy carbonate	liquid	none	38(100)	NA
PEROXYDI-CARBONATES	di(n-propyl) peroxy-dicarbonate	solution	OMS	-23(-10)	-7(20)
	di(sec-butyl) peroxy-dicarbonate	solution	OMS	-10(14)	10(50)

TABLE 6 (CONT'D)

FAMILY NAME	PEROXIDE NAME	FORM	DILUENT	MAXIMUM STORAGE TEMPERATURE °C(°F)	SADT[1] °C(°F)
	Di-2-ethylhexyl peroxy-dicarbonate	solution	OMS	NA	NA
TERTIARY ALKYL HYDRO-PEROXIDES	2,5-dihydro-peroxy-2,5-dimethyl-hexane	white crystals	water	38(100)	60(140)
	cumene hydro-peroxide	liquid	parent hydro-carbons	38(100)	82(180)
	t-butyl hydro-peroxide	solution	t-butanol water	38(100)	>80(176)
PEROXY-KETALS	1,1-di-(t-butylperoxy)-cyclohexane	liquid	butyl benzyl phthalate	32(90)	65(149)
	2,2-bis-(t-butylperoxy)-butane	liquid	dioctyl phthalate	38(100)	82(180)
	1,1-di-(t-amylperoxy)-cyclohexane	liquid	butyl benzyl phthalate	38(100)	80(176)
	2,2-di-(t-amylperoxy)-propane	solution	OMS	38(100)	NA
DIACYL PEROXIDES	diacetal peroxide	liquid	dimethyl phthalate+ isobutyl isobutyrate	NA	NA
	diisonon-anoyl peroxide	solution	OMS	-10(14)	27(80)

TABLE 6 (CONT'D)

FAMILY NAME	PEROXIDE NAME	FORM	DILUENT	MAXIMUM STORAGE TEMPERATURE °C(°F)	SADT[1] °C(°F)
PEROXY-ESTERS	α-cumyl peroxy-neodecanoate	solution	OMS	-18(0)	15(59)
	t-amyl peroxy-neodecanate	solution	OMS	-10(14)	25(77)
	t-amyl peroxy-2-ethyl-hexanoate	solution	phthalate plasticizers	10(50)	45(113)
	t-butyl peroxy-neodecanoate	solution	OMS	-10(14)	27(80)
	t-butyl peroxy-2-ethyl-hexanoate	solution	dioctyl phthalate	18(65)	>54(129)
	2,5-dimethyl-2,5-di(2-ethyl-hexanoylperoxy) hexane	solution	OMS	38(100)	77(170)
	oo-t-butyl o-isopropyl monoperoxy-carbonate	solution	OMS	38(100)	57(135)
KETONE PEROXIDES	methyl ethyl ketone peroxide	solution	MEK[5], or dimethyl-phthalate	38(100)	65(149)
	2,4-pentane-dione peroxide	solution	MEK	38(100)	549!@(0

1. Self-Accelerating Decomposition Temperature
2. Odorless Mineral Spirits
3. Information not available
4. Butyl Benzyl Phthalate
5. Methyl Ethyl Ketone

empirical approach to making these correlations. Using a large data base, Salame [4] was able to determine a simple correlation between measured values of mass loss from standard bottles, certain properties of the permeant molecules, and certain properties of the polyethylene resin used in the bottles. This approach is known as the "Permachor" scheme. A series of reports prepared by the National Institute of Standards and Technology (NIST) [5-10] for the DOT OHMT describe in detail the use of this scheme. A brief review of this approach is presented here.

The rate at which a particular molecule permeates through polyethylene has been found to depend upon various properties of the permeant such as size, shape, polarity and other factors. Attempts to correlate permeation factors (P) with any one property of the permeant were found to give rise to a wide scatter of the data points. However, for the non-polar homologous series of straight chain hydrocarbons a plot of the P-factors verses the number of carbon atoms in the permeant was found to yield a straight line of slope 0.22 on a semilog plot (Figure 2). It can be seen that by increasing the number of carbon atoms in the chain from five (pentane) to eighteen (octadecane) the permeation factor decreases by about two and one half orders of magnitude. Working from this curve, numerical values were empirically assigned to other atoms and organic radicals so as to force the permeability points of other homologous series to fall on the same straight line. For example, it was found that the homologous series of unsaturated hydrocarbons, when plotted on a similar semilog plot, fell on a straight line having the same slope, but was shifted to the right by a factor of 0.2. By assigning a value of - 0.2 to the double bond the P-factors of the unsaturated hydrocarbons fell on the same line with the saturated hydrocarbons. Using all of the permeability data for the different types of organic liquids, both polar and non-polar, a value was assigned to each of them by noting the distance they were shifted from the original line when plotted against the number of carbon atoms in each molecule. First, the number of carbon atoms in the compound being studied was totalled and then the difference between this value (using unity as the value for carbon) and the value required to shift the point onto the original base line was then the number assigned to the particular type of molecule under consideration. This number is referred to as the Permachor (π) value of the molecule. A representative sample of these values is given in Table 7.

Once a Permachor value had been established for each of the various permeants it was found that the same Permachor which had been derived from the 21°C(70°F) data could be used at any other temperature and still yield a straight line relationship between the P-factor and Permachor and with the same value of slope 0.22. An example of this is shown in Figure 3 for two temperatures where the P-factors of over 70 organic liquids have been used in the plot. The equation that fits the two lines is:

$$\log P = K - 0.22\pi \quad (1)$$

where: P is the permeability factor of the liquid permeant, K is a constant which depends on temperature alone, and π is the Permachor value. In the

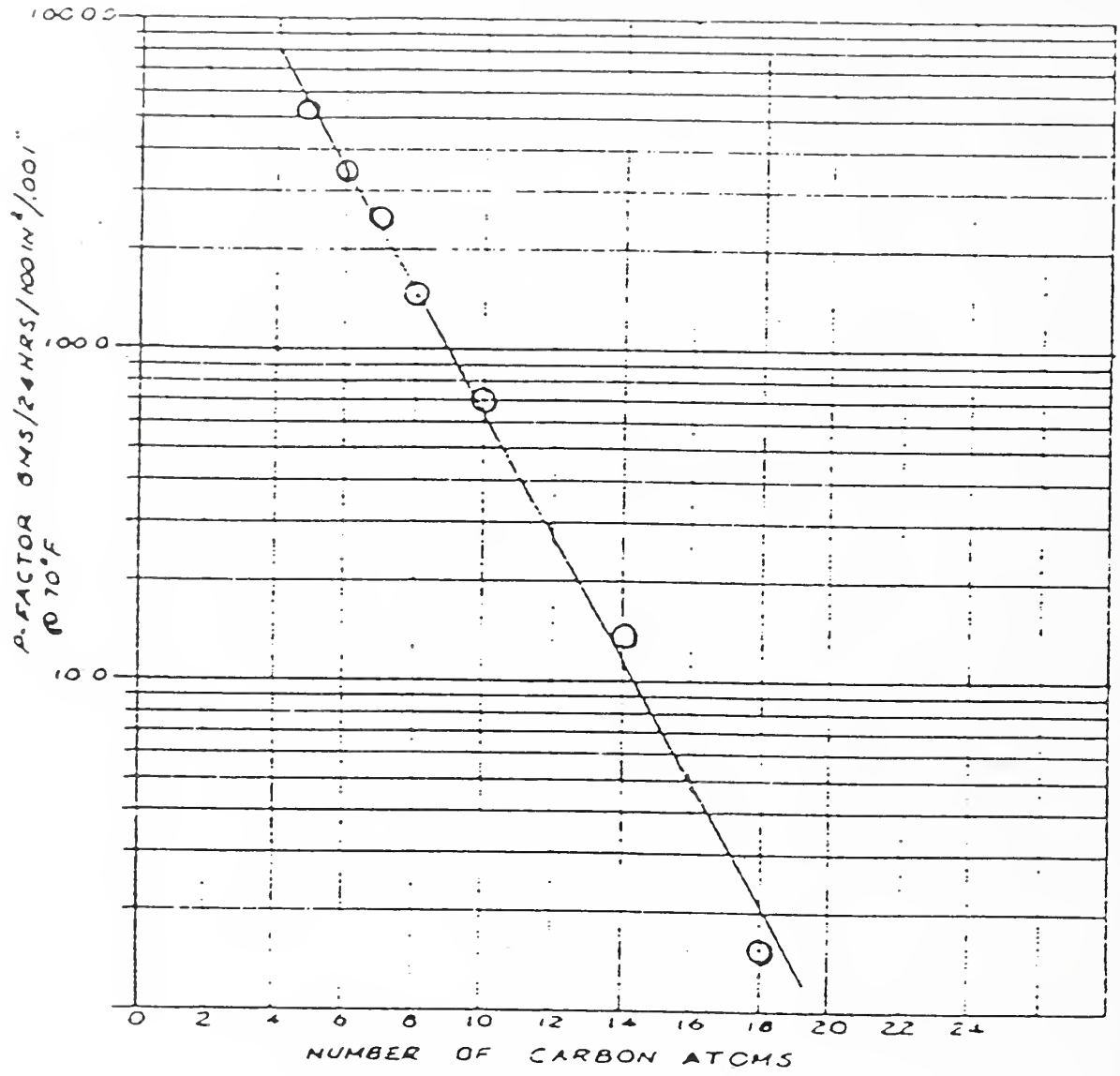

Figure 2. Permeability of Normal Alkanes Versus the Number of Carbon Atoms in the Chain at 21°C(70°F). (Figure Reproduced from Reference [4].)

TABLE 7[1]

PERMACHOR (π) VALUES FOR ESTIMATING P-FACTORS

Atom or Group	Number of Carbon Atoms									
	1	2	3	4	5	6	7	8	9	10
Carbon (--C--)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ether (--O--)	-	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Ester (-C-O-)	-	9.6	9.6	8.0	7.0	7.0	7.0	3.1	3.1	3.1
Ketone (-C-R)	-	10.8	10.8	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Aldehyde (-C-H)	17.8	12.0	12.0	9.5	9.5	8.0	8.0	8.0	8.0	8.0
Anhydride (-C-O-C-)	-	15.8	15.8	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Amide (-C-NH-)	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Amine($--NH_2$)Aliphatic	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Amine Aromatic	-	-	-	-	-	11.0	11.0	11.0	11.0	11.0
Alcohol(--OH)Aliphatic	16.5	16.5	15.5	14.0	14.0	11.0	11.0	10.0	10.0	10.0
Alcohol Aromatic	-	-	-	-	-	13.0	13.0	13.0	13.0	13.0
Acid(-C-OH) Aliphatic	18.0	13.5	13.5	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Acid Aromatic	-	-	-	-	-	14.0	14.0	14.0	14.0	14.0
Phenyl Benzene	-	-	-	-	5.4 below 80°F, 7.6 above 80°F					
Monosubstituted	-	-	-	-	-	5.4	5.4	5.4	5.4	5.4
Disubstituted, ortho, meta, para,	3.8 below 80°F, 5.4 above 80°F									
Iso subst. & Side branching	Add 2.0									
Double Bond Between Carbons	Subtract 0.2									

[1] Values reproduced from reference [4]

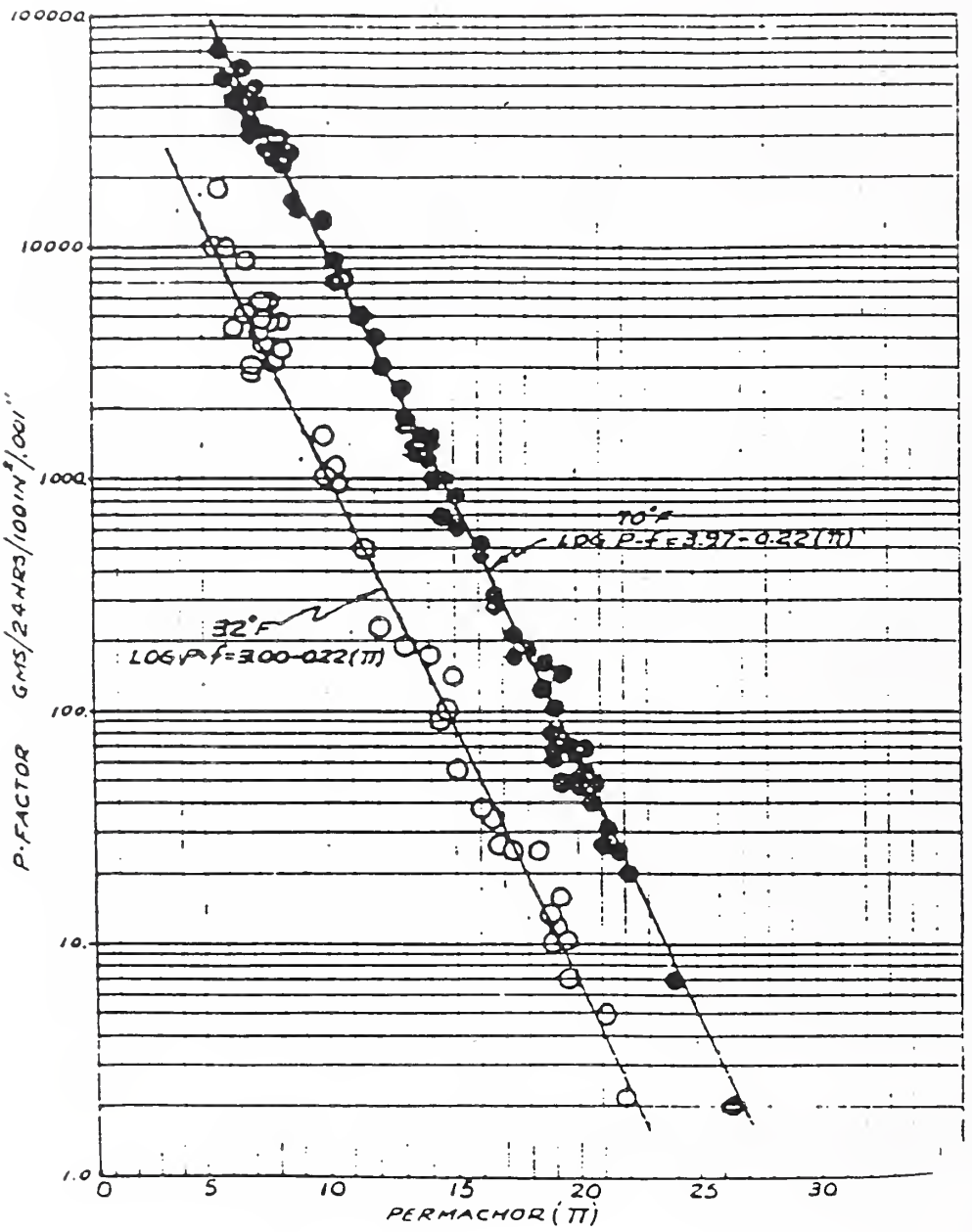

Figure 3. Permeability Versus Permachor Number for Low Density Polyethylene at 0°C(32°F) and 21°C(70°F). (Figure Reproduced from Reference [4].)

original work, the P-factor was expressed in (gm/24 hrs/100 in^2/0.001 in). Further work suggested that the constant K in equation (1), which for a given temperature is the intercept of the line in Figure 3 along the abscissa, was related to the absolute temperature by the equation:

$$K = 16.55 - 3700/T \quad (2)$$

where T is in degrees Kelvin.

In another earlier work [11] it was found that the permeability factor could be related to the temperature as:

$$P = P_0 e^{-E/RT} \quad (3)$$

where P is the permeability factor, P_0 is a constant, E is an apparent activation energy, R is the Universal Gas Constant, and T the absolute temperature. It was further found, for a given permeant, that E could be determined from the empirical formula:

$$E = 0.0348V + 0.75V/L + 2.4\ \Delta H' \quad (4)$$

where V is the molecular volume and L is the molecular length, as determined from measurements using Fisher-Hirschfeld models. $\Delta H'$ is a constant related to the heat of vaporization of the permeant and represents a measure of the polarity.

Reproduced in Table 8 is a representative sample of both calculated and experimentally determined P-factors for organic liquids in polyethylene at three different temperatures. It can be seen that the compounds having the smallest Permachor number are the organic solvents such as benzene and toluene, and the low numbered hydrocarbons from C_5 through C_{10}. Correspondingly, these compounds also have the highest permeation rates through polyethylene. At a temperature of 21°C(70°F), which corresponds to one of the temperatures at which the required testing is done, the experimentally determined P-factors are in rather good agreement with the values calculated using the Permachor scheme.

With respect to the organic peroxides, it should be noted that in Table 8 there is no entry corresponding to the peroxy linkage. However, examination of the molecular structure of many of the organic peroxides currently being shipped in polyethylene packagings suggests that very few are likely to have a Permachor number less than about 20, which is larger than most of the values listed in Table 8. Correspondingly their P-factors should be rather small. As an example of a peroxide having a relatively small Permachor number, we shall consider the compound tertiary-amyl peroxyacetate which has the following molecular structure:

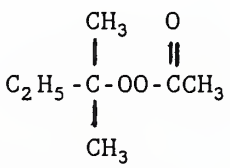

TABLE 8[1]

CALCULATED AND EXPERIMENTAL P-FACTORS FOR A REPRESENTATIVE SAMPLE OF ORGANIC COMPOUNDS IN POLYETHYLENE AT THREE TEMPERATURES

PERMEANT	PERMA-CHOR	P-FACTOR[2] 0°C(32°F) EXP.	0°C(32°F) CALC.	21°C(70°F) EXP.	21°C(70°F) CALC.	54°C(130°F) EXP.	54°C(130°F) CALC.
Pentene-2	4.8	180	90	695	800	16000	15000
n-Pentane	5.0	97	80	526	740	15000	14000
1.1,1 tri-chloroethane	5.6	--	60	260	550	--	10000
Benzene	5.4-7.6	45	65	440	600	4500	3800
n-Hexane	6.0	48	48	350	450	9000	8500
Toluene	6.4	58	40	505	370	5775	7000
p-Xylene	5.8-7.4	85.7	40	486	500	4800	4100
n-Heptene	6.8	--	32	270	300	--	5600
n-Heptane	7.0	48.6	29	270	270	2650	5000
Methyl-cyclohexane	7.0	--	29	275	270	--	5000
Cyclo-Hexane	7.0-8.0	31.6	29	251	270	3730	3100
n-Decane	10	9.5	6.3	71.2	59	1220	1120
Methyl ethylketone	12.5	3.7	1.8	12.6	17	326	320
Tetra-decane	13	1.7	1.4	14.6	13	404	250
n-Butyl-acetate	13	--	1.4	15	13	--	250
Butyr-aldehyde	13.5	0.9	1.0	10	10	584	190

TABLE 8(CONT'D)

PERMEANT	PERMA-CHOR	P-FACTOR[2] 0°C(32°F) EXP.	0°C(32°F) CALC.	21°C(70°F) EXP.	21°C(70°F) CALC.	54°C(130°F) EXP.	54°C(130°F) CALC.
Acetone	13.8	1.4	0.9	6.8	8.5	184	160
Acetic acid	15.5	0.35	0.39	3.1	3.6	66	69
Nitro-methane	16.4	--	0.24	2.1	2.3	--	45
Octadecane	16.7	--	0.2	1.8	2.0	--	40
n-Butyl-alcohol	18	0.10	0.11	0.46	1.0	20.4	20
n-Propyl-alcohol	18.5	0.07	0.07	0.5	0.8	22.4	15
Dibutyl-phthalate	20.9	--	0.02	--	0.23	5.7	4.5

[1] Values reproduced from reference [4].
2 in units of g/24 hrs/100 in^2/0.001 in.

Of the organic peroxides, this molecule represents one of the simplest structures. From Table 8, if we assume that the peroxide linkage and the C=O can be approximated by one ester and one ether linkage, the π value for this molecule is 16.4. At 21°C(70°F) the P-factor is then 2.36, which places this compound at about the same location in the table as nitromethane.

An alternative, although analogous, approach to the Permachor scheme just described has also been suggested [8,10]. This approach involves the idea of an Effective Carbon Atom Number, n_e. As in the Permachor scheme, the n_e is also a shift factor that relates the loss rate of a given permeant to that of some standard or reference permeant. Again, the homologous series of normal hydrocarbons is used as the reference permeants. The principal difference between the two schemes is that in the Permachor method only the number of carbon atoms is counted, whereas in the Effective Carbon Atom Number approach all the atoms in the backbone of the chain, N_A, are considered except end groups such as CN, NH_2, OH, etc. The determination of n_e can be expressed mathematically as:

$$n_e = \log(\dot{Q}_A/\dot{Q}_0)/k \qquad (5)$$

where $\dot{Q}_A$ is the loss rate for a given permeant, and $\dot{Q}_0$ and k are parameters which are determined from the loss rate equation for the normal hydrocarbons, i.e.

$$\log \dot{Q} = \log \dot{Q}_0 + kN_A \qquad (6)$$

If $\log \dot{Q}_A$ is plotted versus n_e, then this method also gives a masterecurve which can be represented by a straight line, as is shown in Figure 4.

(8) THE EFFECT OF DENSITY ON PERMEATION IN POLYETHYLENE

It was noted earlier in Section (4), paragraph 1 that the rate of permeation through polyethylene depends upon the density of the polymer. This effect comes about as a result of the semicrystalline nature of polyethylene. It is generally agreed that the permeant most readily penetrates the disordered or amorphous fraction of the polymer. Thus the higher the density, the higher the percent crystallinity, and the smaller is the permeation rate. This effect is demonstrated in Figure 5, where the permeation rate is plotted versus the density. It can be seen that in going from low density to high density polyethylene the permeation rate decreases by nearly a factor of six. This is also evident in Figure 4 where the data represented by the mastercurves were determined for two types of polyethylene bottles. The density of the low

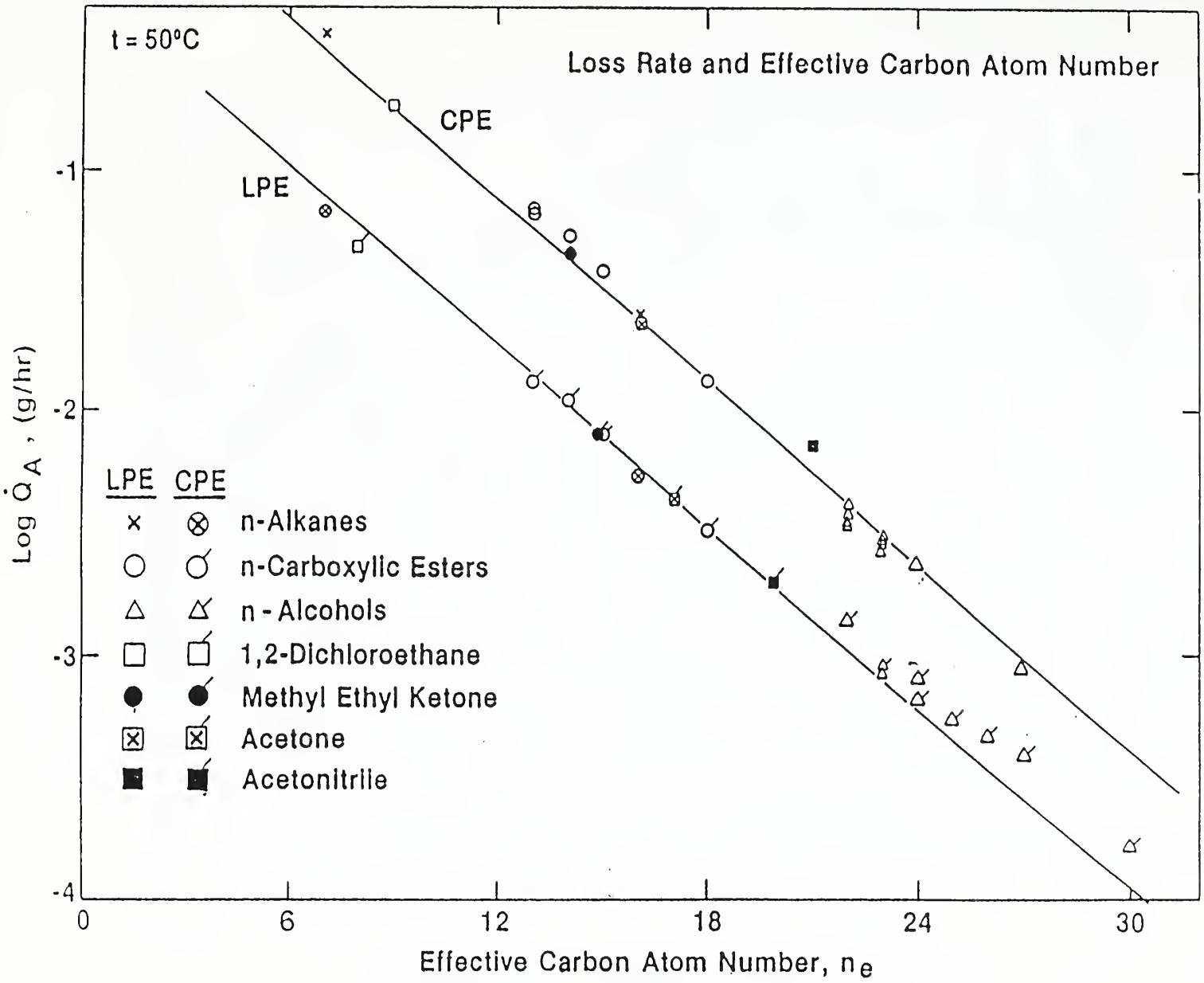

Figure 4. Log Loss Rate of a Given Permeant Versus Effective Carbon Atom Number for Various Permeants in High Density Polyethylene (LPE) and Low Density Polyethylene (CPE). (Figure Reproduced from Reference [10].)

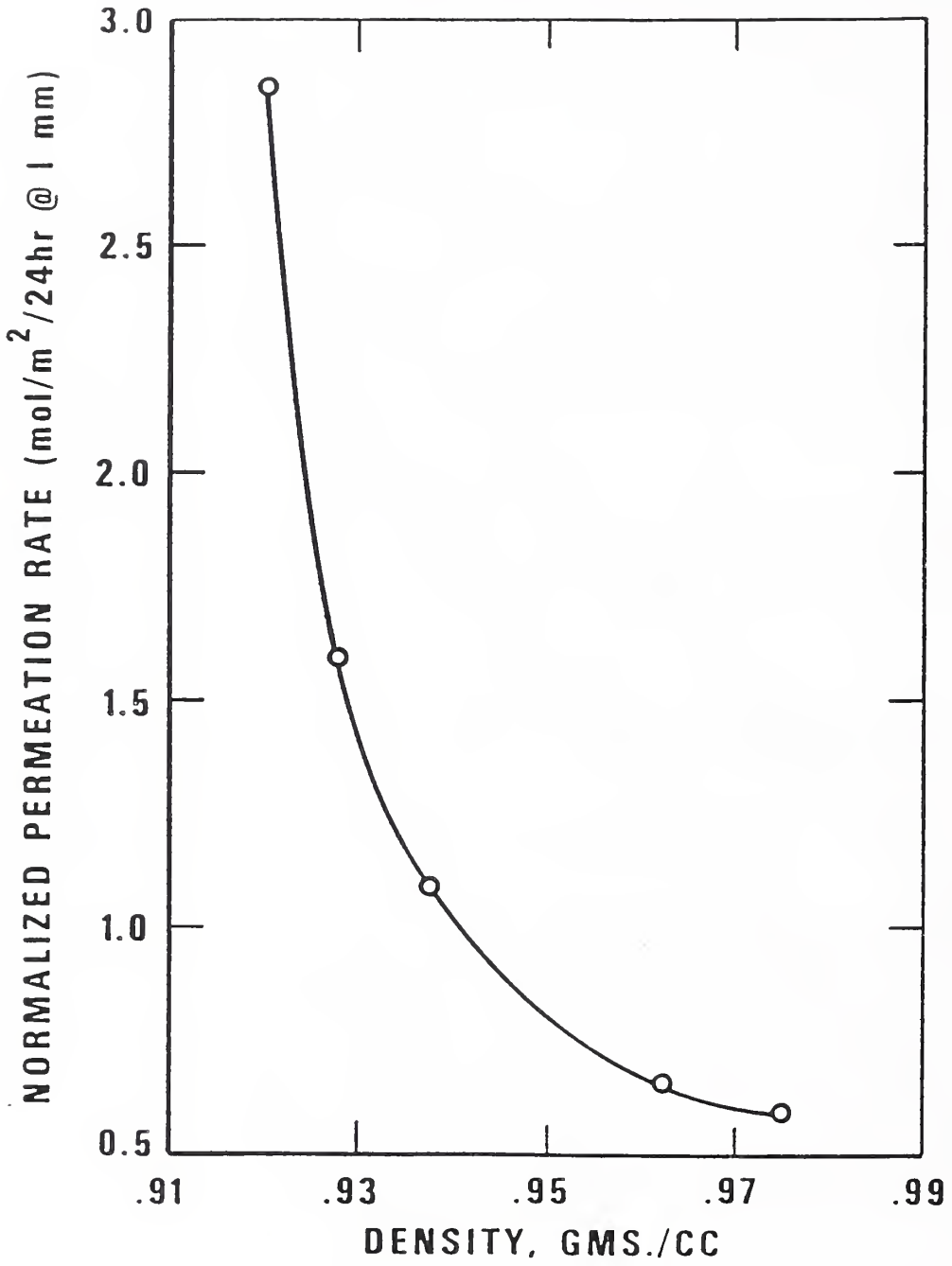

Figure 5. Permeation Rate as a Function of Density: Benzene and Polyethylene (Figure Reproduced from Reference [8].)

density polyethylene was 0.924 ± 0.001 g/cm^3, whereas that of the high density polyethylene was 0.945 ± 0.001 g/cm^3. In this particular case, an increase in density of about 0.021 g/cm^3 is equivalent to increasing the Effective Carbon Atom Number by about three. In the earlier work cited in reference [4], most of the data were obtained from tests done on what is referred to as " regular" polyethylene. However, the K factor in equation (2) was found to vary at 22.5°C(73°F) from 3.21 to 4.05 depending upon the type of polyethylene used. In determining a standard procedure for ranking a potential lading with respect to a standard liquid the density of the polyethylene used for the test packaging is an important consideration.

(9) THE QUESTION OF "STANDARD LIQUIDS" FOR COMPATIBILITY TESTING

In order to determine the feasibility of substituting a standard liquid for a particular hazardous lading it is important to consider each of the three categories of chemical agents mentioned above under Section (5) which can adversely affect the mechanical performance of polyethylene. For substances which cause severe cracking in polyethylene under stress, the European regulations specify the use of a wetting agent. However, the composition is not specified. One person's wetting agent may not be the same as another's. In the United States the compound nonylphenoxy poly(ethyleneoxy) ethanol has been, and appears to remain, the substance of choice as a stress-cracking agent for polyethylene. Both ASTM tests for the environmental stress-crack resistance of polyethylene (D1693 and D2561 [12]) specify the use of this compound either at full strength or as a 10 percent solution in water.

In the case of oxidizing agents nitric acid presents a highly aggressive environment for polyethylene. In polymer research on semicrystalline polymers nitric acid, in combination with high temperature, is commonly used as an etching agent to strip away the amorphous fraction of the polymer leaving the crystalline regions exposed.

The question of standard liquids for permeation testing presents a more complex situation. Current European regulations authorize the use of either normal butyl acetate or a mixture of hydrocarbons (white spirit) depending upon the extent to which the proposed lading swells polyethylene. However the composition of the mixture of hydrocarbons is not specified. White spirit (also known as mineral spirits, petroleum benzin, petroleum ether, benzin, and naphtha) is a highly flammable mixture which consists mainly of hydrocarbons of the methane series, principally pentanes and hexanes,and may also contain from 16-18 percent aromatics. Mineral oil is also a mixture of liquid hydrocarbons. The density of the "light" oil is in the range 0.830 - 0.860 g/cm^3; the "heavy" 0.875 - 0.905 g/cm^3. Both mixtures contain hydrocarbons which span the range of reference materials used in establishing the Permachor and Effective Carbon Atom Number schemes. The odorless mineral spirits commonly used as the diluent for organic peroxides is, presumably, a mixture consisting mainly of the less volatile hydrocarbons in the range from $C_{14}H_{30}$ to $C_{20}H_{42}$. With respect to the current DOT regulations there is a potential problem using the white spirit specified under European regulations since its flash point need be no higher than 61°C and DOT regulations allow for testing to be done at a temperature as high as 60°C.

On the assumption that the Permachor and/or Effective Carbon Atom Number schemes are valid it would then appear feasible that in certain cases one or more standard liquids can be substituted for a potential lading. An essential element of such a scheme is that the Permachor number or Effective Carbon Atom Number of the potential lading be larger than that of the standard liquid, or that its permeation factor be smaller. This scheme appears to be most applicable in the case of pure liquids for which the Permachor numbers can be established or the permeation factors are known. If the Permachor number of the potential lading is larger than that of the standard liquid, or alternatively its permeation factor smaller, then it would qualify to be placed in the group for which the standard liquid can be substituted. If the reverse is true, then the testing should be done using the potential lading. Classes of pure liquids or new liquids for which there is no well established data base on their permeability should be subjected to a compatibility test. The question of mixtures will be dealt with later on.

(10) STANDARDIZED BOTTLE TEST FOR RANKING POTENTIAL LADINGS

Up to this point the discussion has been centered on the possibility of qualifying groups of potential ladings by the use of one or more standard liquids in tests for compatibility. The question of what method, or methods, should be used to rank a potential lading with respect to the standard liquid is also of relevance to this report. In reference [8] considerable attention was given to the screening of ladings and materials, as well as to standardized methods for compatibility testing. It was concluded that in the area of permeation a reference material in the form of a small bottle might be very useful. Both the advantages and disadvantages of bottle tests were discussed in reference [8], and procedures for the establishment of a standardized permeation measurement system were also presented. Discussions with industry representatives indicate that bottle tests are currently in rather widespread use. In the interest of time savings, these tests are generally carried out at elevated temperatures. If the bottles are carefully designed and are manufactured to strict specifications, a standardized bottle test should provide a satisfactory means for ranking the permeability of prospective ladings with respect to a set of standard liquids. One very important consideration in the selection of materials to be used in the processing of the bottle is density. Depending upon the type of packaging to be manufactured, the density of the resin used to produce the packaging may vary from about 0.920 to about 0.955 g/cm^3. As noted earlier, the permeability of polyethylene depends rather strongly on the density. There are then two aspects to permeability testing which should be addressed. In the generic sense, as a method of ranking potential ladings with respect to a particular standard liquid, the use of a standard bottle/bottles appears feasible. Two different standard bottles would be appropriate, one processed from a resin in the low density range, and one from a resin in the high density range. Such a scheme provides a means for comparing, on a more quantitative basis, the extent of permeation through polyethylene of a large number of different chemical compounds. On the other hand, the density of a given packaging may be different from that of either of the standard bottles.

It is important, therefore, in determining the compatibility of a packaging with a given lading to carry out the tests using a bottle which has been manufactured to have as closely as possible the same characteristics as the actual packaging, including its density.

(11) MIXTURES

Mixtures may represent one of the most troublesome cases where compatibility testing is concerned. This comes about as the result of one or more of several possibilities. Many active liquid chemicals are not shipped as pure liquids but are shipped as solutions containing both active chemicals and ingredients which may be labelled as inert. In some cases the so-called "inert ingredients" may contain surfactants or other possible stress-cracking agents. While the active chemical ingredients may be compatible with polyethylene the inert ingredients may not be. It is also possible that a liquid diluent may cause swelling of the polyethylene or permeate through it. A third possibility can arise if the two active chemical ingredients, which individually are compatible with the packaging, when combined may have a synergistic effect leading to incompatibility. If one or more of these situations is a possibility, then the Permachor or Effective Carbon Atoms Number scheme may not be applicable unless the permeabilities of each individual ingredient and their combinations have been determined. Therefore, in the case of mixtures which have not previously been tested, or those for which all of the ingredients are not specified, testing both with a standard bottle and the full sized packaging would appear to be appropriate.

(12) CONTACTS WITH INDUSTRY REPRESENTATIVES

Contact was made with nineteen of the major manufacturers of polyethylene packagings and organic peroxides. Each company was asked six or more of the following questions:

(1) As a manufacturer and/or shipper of organic peroxides does your company do your own compatibility testing of your products with polyethylene packagings or do you rely on the container manufacturer for such tests?

(2) What tests do your company use to determine the compatibility of organic peroxides which are unstable at 70°F?

(3) What diluents are being used by your company in the transportation of organic peroxides?

(4) If liquids such as mineral spirits or mineral oil are being used as a diluent, is the composition of the diluent specified?

(5) Can your company provide information, or is information available, on the permeation of mixtures of organic peroxides and their diluents through polyethylene packagings of different densities?

(6) Does your company conduct tests for compatibility using small blow molded polyethylene bottles (8 to 16 oz)?

(7) If your company conducts bottle tests, do you manufacture your own bottles?

(8) If your company conducts bottle tests, would a standard reference material polyethylene bottle/bottles for industry wide use be of interest or of value to your testing program?

As of the date of this report there have been eight responses either by letter or by telephone. A summary of these responses is presented here.

(A) The container manufacturers generally do compatibility testing as a service to their customers. The peroxide manufacturers perform more limited compatibility tests, generally when a new solution or packaging is encountered.

(B) In the case of peroxides which are unstable at 70°F, the majority responded that they either do not have a test for these materials, or that they would not ship such materials in polyethylene containers. One company responded that such materials are tested under typical storage conditions.

(C) Among the numerous liquids being used as diluents, the following were listed: Various brands and grades of odorless mineral spirits, white mineral oil, ethylbenzene, butyl benzyl phthalate, bis (2 ethylhexyl)-phthalate, phthalate esters, esters of succinic, glutaric and adipic acids, complex esters, 2-ethylhexlyacetate, methyl ethyl ketone and water.

(D) Two commercially available products having the name mineral spirits or white mineral oil were identified as commonly used diluents. One product, identified as odorless mineral spirits, was described as being a mixture of hydrocarbons having a density of 0.759 g/cm^3 at 60°C. The second product, white mineral oil, was described as having a density of 0.875 g/cm^3 at 60°C, but its composition was not specified.

(E) The companies responding were able to provide only very limited information concerning the permeation of organic peroxides and their diluents through polyethylene.

(F) The container manufacturers responded that they do conduct bottle tests or, in some cases, use other test methods. Bottle tests are usually conducted using small blow molded bottles, generally 16 oz. In some cases they also provide such bottles to their customers.

(G) Most of the companies contacted do not manufacture their own test bottles.

(H) With regard to the matter of a standardized bottle for permeability testing, two companies responded that such procedure might be somewhat impractical since there are so many different polyethylene resins currently in use. However, an industry wide standard on the specifications of the bottle was considered much more important, especially in the areas shape, size, wall thickness, uniformity of wall thickness and the processing parameters.

(13) RECOMMENDATIONS

Based upon the discussion presented in Sections (1) through (12) there are several recommendations which can be made with regard to testing for the compatibility of liquid chemical ladings with polyethylene. In Section (5), it was pointed out that there are three general classifications of liquid chemical agents which can lead to degradation of the mechanical performance of polyethylene packagings (stress-cracking agents, chemicals which permeate and swell, and strong oxidizers). It is important, therefore, that all three classes of chemicals be addressed in the design of compatibility tests. A fourth mechanism which can result in the degradation of polyethylene is the chemical degradation caused by ultraviolet light. However, this problem can be minimized by the addition to the resin of UV stabilizers and various colored pigments or carbon black. The following recommendations apply to the three classes of chemical agents referred to above:

(i) Stress-cracking agents- A test for Environmental Stress-Crack Resistance (ESCR) is necessary as a means of screening both the polyethylene resin and the container design. Testing of the resin is necessary in order to determine the degree to which a particular polyethylene under consideration is susceptible to stress cracking. Testing of the resin is a material specification of most interest to the container manufacturer and as such need not be part of the regulatory process. Testing of the actual packaging is necessary as it may reveal areas of high residual stress or areas where high stresses may result under relatively low external loads. Insofar as a test for ESCR is concerned, the solution of ten percent nonylphenoxy(polyethyleneoxy)ethanol in water which is currently in widespread use in ESCR testing appears to be one of the most aggressive environments for polyethylene. If a set of standard liquids are to be adopted for compatibility testing, then one of the liquids specified should be a surfactant of the type just described.

ESCR testing is generally carried out at an elevated temperature, as in ASTM D1693 [12], in order to accelerate the time to failure. The Standard Requirements contained in Title 49 CFR under paragraph (173.24d)(2)(b and c) appear to allow for such accelerated testing (28 days at a temperature of no lower that 50°C, or 14 days at a temperature of no lower than 60°C). The current European regulations (ADR marginal 3551 (6)(c)) allow for accelerated testing to a much lesser extent since the storage time specified is only 21 days at 40°C.

(ii) Permeation and swelling- A permeation test is highly important for the screening of potential ladings. The type of test to be used should be

decided based upon the available information concerning the composition of the lading and the permeability of each component of the lading.

(a) In the case of pure liquids the use of a standard liquid appears feasible under the following conditions:

(1) A Permachor or Effective Carbon Atom Number can be established for the lading, or alternatively the permeation factor of the lading is known. If the Permachor or Effective Carbon Atom Number for the lading is larger than that of the proposed standard liquid, or the permeation factor is lower, then the standard liquid could be substituted for the lading under consideration. On the other hand, if the Permachor or Effective Carbon Atom Number is equal to or smaller than that of the proposed standard liquid, then the testing should be done using the actual lading which is to be shipped.

(2) The composition of the standard liquid/liquids is specified. As noted already, current European requirements allow for the substitution of one or more standard liquids depending upon the type of lading to be shipped. However, the composition of the "white spirits" is not specified. We have seen earlier that, in the case of polyethylene, the permeability of the liquid normal hydrocarbons can vary by about three orders of magnitude in going from pentane to octadecane. In order to place the ranking of potential ladings with respect to the standard liquid on a more quantitative basis, the composition of the standard liquid should be specified and should be keep the same.

(3) Current European regulations specify the use of two standard liquids as substitutes which swell and permeate polyethylene, (1) normal butyl acetate (Permachor number = 13), and (2) a mixture of hydrocarbons (Permachor number = ?). These two liquids are considered equivalents for a very large grouping of substances including ethers, aldehydes, ketones, esters, oxygenated substances, halogenated substances, heating oils, and ammonia solutions. The composition of the mixture of hydrocarbons is specified only to the extent that it must have a boiling point in the range from 180 - 200°C, a relative density of 0.79 g/cm^3, a flash point above 61°C, and an aromatic content of 16 - 18 percent (C_9 and higher aromatics only). Further work is needed to insure that the composition range specified is sufficient to insure that the mixture of hydrocarbons will have a Permachor number smaller than (and permeation factor larger), or equivalent to, that of the substances listed in the set of European regulations. There is presently a problem with the use of the mixture of hydrocarbons currently specified which can have a flash point as low as 61°C. Current DOT regulations allow for the compatibility testing to be carried out at a temperature as high as 60°C.

(b) Mixtures present a separate issue. Because of the possible presence of unspecified substances or synergisms resulting from the mixing of two or more chemical compounds, the use of standard liquids should be

more restricted where mixtures are concerned. If the permeation factors for each chemical species in the mixture and the possible synergistic effects of mixing them are known, then the substitution of a standard liquid appears feasible. If not, then each mixture should be tested individually.

(c) Organic peroxides- The organic peroxides, for the most part, represent a special class of mixtures. While some organic peroxides are shipped as pure liquids, most are diluted with one or more of a number of organic liquids. As noted in Table 6 and again in Section (12)(C) the list of commonly used diluents includes mineral spirits, mineral oil, a variety of phthalates, alcohol and water mixtures, phthalic esters, esters of dibasic aliphatic acids, complex esters, methyl ethyl ketone, isobutyl isobutyrate, ethyl benzene, tertiary butyl alcohol, and water.

Insofar as the permeation of the peroxide itself through polyethylene is concerned, it was pointed out in Section (7) that most peroxide molecules are sufficiently bulky that their Permachor numbers are likely to be well in excess of 20. One exception was tertiaryamyl peroxyacetate for which it was estimated that the Permachor number is 16.4. Permeation of the diluent through polyethylene may be a more serious problem. Again, most of the diluents listed above have Permach or numbers in excess of 20 (phthalates and dibasic aliphatic acids for example). However, several do not. These would include ethylbenzene (7.4), methyl ethyl ketone (12.5), isobutyl isobutyrate (15.1), and tertiary butyl alcohol (18).

It is known that the oxidative action of peroxides against polyethylene is acutely dependent upon a variety of compositional and exposure factors which in combination can lead to the deterioration of the mechanical integrity of the polymer. These factors include the degree and type of branching present, degree of crystallinity, transition metal contamination, diffusion coefficients of the peroxide alone or in combination with known polyethylene swelling agents, presence of antioxidents, ultra-violet exposure and temperature. For this reason it is important to determine whether compositional parameters common to the polyethylenes currently used in transportation of organic peroxides and their diluents, in combination with normal transportation conditions, can lead to the mechanical degradation of the packaging.

(d) Standard liquid-If a standard liquid is to be specified for use in a test for the permeation and swelling of polyethylene, its Permachor number should be as small as is practicable in order to accommodate the greatest possible number of substances for which it is to be a substitute. We shall explore this position further by considering the normal alkanes which make up a major component of mineral spirits or mineral oil. Listed in Table 9 are the normal hydrocarbons from n-dodecane ($C_{12}H_{26}$) to n-octadecane ($C_{18}H_{38}$). Included in the table are the permeation-factors, as determined from Figure 2, the Permachor number, determined using equation (1) and a K value of 4.05 at 73°C, and the density at room temperature. The

Permachor numbers range from 12 to 17, the average value being 13.6 which corresponds very closely to n-tetradecane ($C_{14}H_{30}$). At the same time the density ranges from a low value of 0.749 g/cm^3 for n-dodecane to 0.777 g/cm^3 for n-octadecane, the average value for the series being 0.764 g/cm^3 (n-tetradecane). It was mentioned in Section (12)(D) that two commercial products which are commonly used as diluents were referred to as odorless mineral spirits and white mineral oil. The density of the odorless mineral spirits was reported to be 0.759 g/cm^3 which is close to the average value for the series of n-alkanes described above. On the other hand, the density of the white mineral oil was reported to be 0.875 g/cm^3, a value considerably higher than those for the n-alkanes which are

TABLE 9

PERMEATION-FACTORS, PERMACHOR NUMBERS, AND DENSITY FOR SOME OF THE NORMAL ALKANES

Hydrocarbon	PERMEATION FACTOR[1]	PERMACHOR NUMBER[2]	DENSITY[3]
Dodceane	26.0	12.0	0.749
Tridecane	18.0	12.7	0.756
Tetradecane	11.0	13.7	0.763
Pentadecane	7.4	14.5	0.769
Hexadecane	4.7	15.4	0.773
Heptadecane	3.3	16.0	0.778
Octadecane	2.0	17.0	0.777

[1] Obtained from Figure 2
[2] Determined using equation (1)
[3] g/cm^3

solids at room temperature. In order to achieve a density value as high as 0.875 g/cm^3 we can only speculate that this formulation contains a significant fraction of aromatic compounds. Except for the low numbered hydrocarbons which are highly volatile, the average Permachor number of any combination the liquid hydrocarbons is likely to be higher than that of several of the examples cited above which are used as diluents for peroxides (ethyl benzene and methyl ethyl ketone for example). Again, one can speculate that the presence of aromatics is intended to account for these highly permeable diluents, as in the standard liquid mixture of hydrocarbons specified in the European regulations.

(iii) Oxidizing agents- In the event that oxidizing agents other than organic peroxides be transported in polyethylene packagings, a strong oxidizing agent such as nitric acid appears feasible as a standard test liquid. European regulations stipulate that a 55 per cent concentration of nitric acid is to be used. However, if the lading is more strongly oxidizing than the 55 per cent solution of nitric acid, then the testing is to be done using the actual lading to be shipped.

(14) FUTURE WORK

Although the feasibility of the Permachor method has been demonstrated, more work is needed to establish its reliability when applied to the large class of hazardous materials currently transported in polyethylene packagings. This is particularly true for the class of liquid organic compounds which both swell and permeate through polyethylene. If a standard liquid is to be used, then its Permachor number must be smaller than, or equal to, that of the prospective lading. Current European regulations specify two standard liquids as substitutes for liquids which swell and permeate through polyethylene, (1) normal butyl acetate (Permachor number = 13), and (2) a mixture of hydrocarbons (Permachor number = ?). These two liquids are considered equivalents for a very large grouping of substances including ethers, aldehydes, ketones, heating oils, hydrocarbons, halogenated substances, oxygenated substances, esters, and ammonia solutions. The composition of the mixture of hydrocarbons is specified only to the extent that it must have a boiling point in the range from 180-200°C, a relative density of 0.79 g/cm^3, a flash point above 61°C, and an aromatic content of 16 - 18 percent (C_9 and higher aromatics only). Further work should be done to determine whether the composition range specified is sufficient to insure that the mixture of hydrocarbons will have a Permachor number smaller than (and permeation factor larger), or equivalent to, that of the substances listed in the European regulations or other substances which may be encountered in the transportation system. Of particular interest are those compounds within each group which have relatively low molecular weights and high permeation factors. One problem concerns the use of a standard liquid which has a flash point of 61°C. Current DOT regulations allow for the compatibility testing to be carried out at a temperature as high as 60°C. It may be necessary to specify at least two standard mixtures of hydrocarbons depending upon the test temperature.

With regard to the organic peroxides, it is known that the oxidative action of peroxides against polyethylene is acutely dependent upon a variety of compositional and exposure factors which in combination can lead to deterioration of the mechanical integrity of the polymer. These factors include the degree and type of branching present, degree of crystallinity, transition metal contamination, diffusion coefficients of the peroxide alone or in combination with known polyethylene swelling agents, presence of antioxidants, ultra-violet exposure and temperature. For this reason it is important to determine whether compositional parameters common to the polyethylenes currently in use in the transportation of organic peroxides and their "inert" ingredients, in combin- ation with normal exposure conditions, can lead to the mechanical degradation of the packaging. Further work should be done to evaluate the need for future concern regarding the peroxide induced oxidation of polyethylene packagings and if necessary propose guidelines which can be used to predict the compatibility of organic peroxides with polyethylenes used for packagings. Such work should include controlled oxidation experiments of candidate peroxides and diluents to determine the extent of oxidation and degradation of the mechanical properties under conditions of time and temperature likely to be encountered in transportation and storage.

REFERENCES

[1] Code of Federal Regulations, Title 49, Parts 100 to 177 and Parts 178 to 199. Published by the Office of the Federal Register, National Archives and Records Administration. These documents are available through the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

[2] ADR Appendix A.5, European Regulations Governing General Packing Conditions, Types of Packaging, Requirements Applicable to Packaging, Test Requirements for Packagings.

[3] Figure reproduced from reference [5].

[4] Salame, M., An Empirical Method for the Prediction of Permeation in Polyethylene and Related Polymers, SPE Transactions, 1, No. 4, pp. 1-11 (1961).

[5] Crissman, J.M., C.M. Guttman, and L.J. Zapas, Performance of Plastic Packaging for Hazardous Materials Transportation, Part I, Mechanical Properties, Report No. DOT/MTB/OHMO-76/4, October 1976. This report is available from the National Technical Information Service, Springfield, VA 22151.

[6] Barnes, J.D., and G.M. Martin, Performance of Plastic Packaging for Hazardous Materials Transportation, Part II, Permeation, Report No. DOT/MTB/OHMO-76/5, October 1976. This report is available from the National Technical Information Service, Springfield, VA 22151.

[7] Crissman, J.M., and L.J. Zapas, Performance of Plastic Packaging for Hazardous Materials Transportation, Part III, Stress Cracking, Report No. DOT/MTB/OHMO-77/4, December 1977. This report is available from the National Technical Information Service, Springfield, VA 22151.

[8] Barnes, J.D., G.M. Martin, and F.L. McCrackin, Performance of Plastic Packaging for Hazardous Materials Transportation, Part IV, Standardizing Permeation Measurements, Report No. DOT/MTB/OHMO-77/5, June 1979. This Report is available from the National Technical Information Service, Springfield, VA 22151.

[9] Crissman, J.M., L.J. Zapas, and G.M. Martin, Performance of Plastic Packaging for Hazardous Materials Transportation, Part V, Mechanical Properties, Report No. DOT/MTB/OHMO-80/2, December 1979. This report is available from the National Technical Information Service, Springfield, VA 22151.

[10] Phillips, J.C., Performance of Plastic Packaging for Hazardous Materials Transportation, Part VI, Report No. DOT/MTB/OHMO-80/3, April 1980. This report is available from the National Technical Information Service, Springfield, VA 22151.

REFERENCES (CONT'D)

[11] Bent, H.A., and J. Pinsky, Theoretical Investigation of the Mechanism of Transfer of Materials through Polyethylene, Wright Air Development Center Technical Report 53-133, Part 2 (1955).

[12] ASTM 1989 Annual Book of ASTM Standards, volume 8.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. ASTM D1693, Standard Test Method for Environmental Stress-Crack Resistance of Ethylene Plastics, page 53; ASTM D2561, Standard Test Method for Environmental Stress-Crack Resistance of Polyethylene Containers.

NIST-114A
(REV. 3-89)

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

BIBLIOGRAPHIC DATA SHEET

1. PUBLICATION OR REPORT NUMBER
NISTIR 4346

2. PERFORMING ORGANIZATION REPORT NUMBER

3. PUBLICATION DATE
May 1990

4. TITLE AND SUBTITLE

Development of Test Methods to Determine the Compatibility of Liquid Hazardous Materials with Polyethylene Packagings

5. AUTHOR(S)

John M. Crissman

6. PERFORMING ORGANIZATION (IF JOINT OR OTHER THAN NIST, SEE INSTRUCTIONS)

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
GAITHERSBURG, MD 20899

7. CONTRACT/GRANT NUMBER
DTRS-57-89-X-00121

8. TYPE OF REPORT AND PERIOD COVERED
Final 6/18/89 - 12/18/89

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (STREET, CITY, STATE, ZIP)

U.S. Department of Transportation
Research and Special Programs Administration
Office of Hazardous Materials Transportation

10. SUPPLEMENTARY NOTES

[ ] DOCUMENT DESCRIBES A COMPUTER PROGRAM; SF-185, FIPS SOFTWARE SUMMARY, IS ATTACHED.

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

This report describes work done for the Department of Transportation, Office of Hazardous Materials Transportation to develop test methods which can be used to determine whether a liquid hazardous material may be shipped in a specific type of polyethylene packaging. Current federal regulations require that each prospective lading be tested individually in proposed polyethylene packagings and do not make provision for liquids which may be unstable at 21°C. One area being explored is the possibility of dividing the liquids into groups and authorizing the transportation of all the liquids in the group based on tests done using one standard liquid from the group. The feasibility of basing compatibility tests on the use of standard liquids is assessed and recommendations are made as to the conditions under which such a scheme can be used. An empirical scheme known as the "Permachor" method for ranking the permeability of liquid hazardous materials is proposed.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

Compatibility; hazardous materials; organic peroxides; permachor; permeation; polyethylene; standard liquid.

13. AVAILABILITY

[X] UNLIMITED

[ ] FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NATIONAL TECHNICAL INFORMATION SERVICE (NTIS).

[ ] ORDER FROM SUPERINTENDENT OF DOCUMENTS, U.S. GOVERNMENT PRINTING OFFICE, WASHINGTON, DC 20402.

[X] ORDER FROM NATIONAL TECHNICAL INFORMATION SERVICE (NTIS), SPRINGFIELD, VA 22161.

14. NUMBER OF PRINTED PAGES
51

15. PRICE
A04

ELECTRONIC FORM