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**SOME CANDIDATE REPLACEMENT MATERIALS
FOR DIOCTYL PHTHALATE
IN "HOT SMOKE" AEROSOL PENETROMETER
MACHINES**

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April 1991

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Aberdeen Proving Ground, Maryland 21010-5423

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PREFACE

The work described in this report was authorized under Engineering Study Proposal (ESP) No. FI-7-8860, "Alternative for DOP," and was completed using OMA funds under in-house Project No. FI-7-8860. This work was started in September 1987 and completed in March 1991.

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Some Candidate Replacement Materials for Dioctyl Phthalate in "Hot Smoke" Aerosol Penetrometer Machines

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For many decades dioctyl phthalate (DOP), a common industrial material, has been used by the U.S. Army and other agencies to simulate aerosol behavior in nondestructive gas mask and filter serviceability testing, and for related test purposes. Techniques are completely standardized. But DOP is now considered to be a potentially hazardous material. The research reported here, which was performed using ATI Q-127 and TDA-100 "hot smoke" aerosol penetrometer test

machines, identified relatively innocuous, inexpensive replacement materials for DOP. One of these, a synthetic hydrocarbon (poly-alpha olefin [PAO]), can be used to replace DOP directly with minimum impact upon existing hardware and procedures. Of more than two dozen candidate replacement materials that were tested, isostearic acid and oleic acid also performed well as DOP replacements. All three materials also show promise for cold smoke testing applications.

INTRODUCTION

Background

Di (2-ethylhexyl) phthalate, also called dioctyl phthalate, di-sec octyl phthalate, DOP or DEHP, is a widely used industrial material. Over 90% of the material produced is used as a plasticizer, primarily for polyvinyl chloride plastics. The properties of DOP that make it useful as a plasticizer, including low vapor pressure, chemical stability, and insolubility in water, also make it useful as a test aerosol. DOP aerosols are used in respirator fit testing, high-efficiency particulate aerosol (HEPA) filter testing, aerosol research, aerosol instrument calibration, and other applications. These uses involve human occupational exposure to sub-micrometer-sized DOP aerosols, often

briefly but in moderately high concentrations (Hinds et al., 1983).

The toxicological properties of DOP and related compounds have been studied often since their use became widespread several decades ago (Shaffer et al., 1945; Calley et al., 1966; Knowles et al., 1987). In 1982, an association was reported between exposures of 3000-12000 ppm of DOP in the diet and the development of hepatocellular carcinomas or neoplastic nodules in mice and rats (NTP, 1982). Although this association has not since been convincingly demonstrated, concern about the potential health threats to people working with DOP test aerosols has led to a search for substitute materials. This search has taken a number of different directions, depending in part upon the specific test applications for which a DOP replacement has been sought. For example, Hinds et al. (1982) looked at size distributions of test aerosols of corn oil, di

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(2-ethylhexyl) sebacate (DOS), mineral oil and polyethylene glycol (PEG) and compared these to DOP. Gerber (1980) has published a detailed study of glycols as safe DOP replacements. Other comparative studies of size distribution and filter penetration of corn oil (Sharaf and Troutman, 1988), mineral oil, PEG, and DOP have been reported (Gerbig and Keady, 1985). Interest has been revived in the use of solid aerosols including salts as test media (Murrow and Nelson, 1973), and their performance has been compared to DOP aerosols.

The U.S. Army routinely performs 100% quality control testing of filter canisters manufactured for use with field-issue gas masks, and periodic sampling and testing of canisters stored in its supply depots. In April 1986, the U.S. Army Surgeon General placed severe restrictions upon testing with DOP; agencies were also informed that dioctyl sebacate (DOS) would no longer be acceptable as a DOP replacement material, and that similar restrictions would apply for both. These restrictions included occupational exposure monitoring of workers exposed to DOP aerosols and liquid, medical surveillance, issue of personal protective equipment, formal notification to workers of associated risks, and labeling of work areas as "cancer suspect agent areas." Clearly, these actions placed severe restrictions upon routine, 100% quality assurance testing of filters and other equipment. For this reason, in 1988 the U.S. Army initiated a detailed study of the problem of finding an acceptable substitute material for DOP that could meet all standard military test specifications while itself being a noncarcinogen and, ideally, having other attributes including acceptable acute inhalation toxicity, low cost, ready availability, and the ability to replace DOP directly in machines at test installations without retrofit or other modification of these machines.

This paper describes the experimental procedures and results of that study which are applicable specifically to "hot smoke"

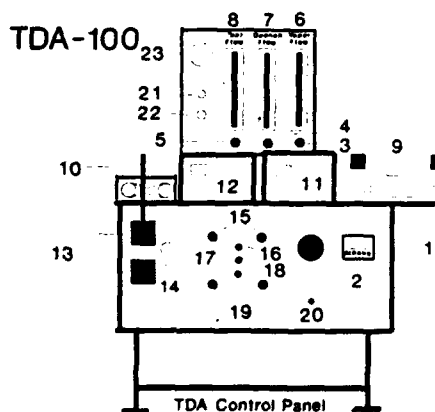
aerosol penetrometer machines including the Army-standard "Q-127" machine that is currently produced as the model TDA-100 by Air Techniques, Inc., Baltimore, MD. The TDA-100 and its controls are shown schematically in Figure 1.

Test Specifications

Present U.S. Army test specifications for acceptable "hot smokes" prescribe a geometric mean diameter (GMD) of between 0.2 and 0.3 μm , with a geometric standard deviation (GSD) ≤ 1.30 , and a mass concentration at the test chuck, where filters are held for penetration measurements, of $100 \pm 20 \text{ mg/m}^3$. The mass concentration of an aerosol in milligrams per cubic meter is given by the equation:

$$\text{mg/m}^3 = \frac{\pi}{6} \times 10^{-3} dND_{\mu\text{m}}^3, \quad (1)$$

FIGURE 1. Schematic representation of Air Techniques, Inc. model TDA-100 machine, including operating controls.



TDA-100 Controls Description

- | | |
|---------------------------|----------------------------|
| 1 Pot Temperature control | 14 Chuck Pressure Gauge |
| 2 Particle Size Control | 15 Chuck Close Control |
| 3 Vapor Flow Valve | 16 Power Indicator Light |
| 4 Quench Flow Valve | 17 Power On Button |
| 5 Test Flow Valve | 18 Power Off Button |
| 6 Vapor Flowmeter | 19 Chuck Open Control |
| 7 Quench Flowmeter | 20 Photometer Switch |
| 8 Test Air Flowmeter | 21 Vacuum Head Valve |
| 9 Mechanical Owl | 22 Vacuum Head Gauge |
| 10 Light Photometer | 23 Filter Resistance Gauge |
| 12 Penetration Indicator | |
| 13 Chuck | |

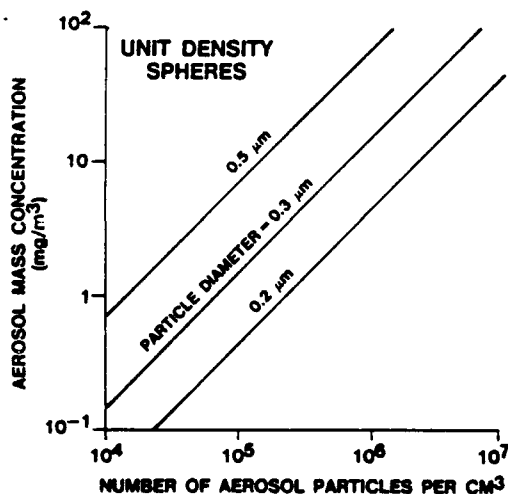
where d (g/cm^3) is the density of the material, N is the aerosol particle population per cm^3 , and $D_{\mu\text{m}}$ is the particle diameter in micrometers. In Figure 2, Eq. 1 is plotted for unit density spheres for three values of the GMD. It can be shown that as the aerosol mass concentration approaches $100 \text{ mg}/\text{m}^3$, the number of $0.3\text{-}\mu\text{m}$ particles per cubic centimeter approaches 7×10^6 , and that this number for $0.2\text{-}\mu\text{m}$ particles is well in excess of 10^7 .

Populations as large as these exceed the operating ranges of laser aerosol spectrometers like the one discussed below that was used in our studies. Typically, these instruments can count 1.7×10^4 particles with 90% accuracy in a one cubic centimeter sample per second. Thus an accurate aerosol dilution of several hundred times is required to count the aerosol delivered to a Q-127 machine canister test chuck at $100 \text{ mg}/\text{m}^3$. In the research reported here, such aerosol dilutions were made routinely using precision equipment as described later in this paper.

TEST EQUIPMENT USED

Our Q-127 machine was a refurbished older model of the similar but redesigned and simplified "monodispersed aerosol pen-

FIGURE 2. Plot of Eq. 1 for unit density spheres.



etrometer" presently being marketed by Air Techniques, Inc. (ATI) under the model number TDA-100 (Figure 1). These machines generate "hot smokes" by the vaporization and recondensation of DOP or other liquids, that have suitable vapor pressure and other physical properties, which are placed in a heated reservoir. Hinds et al. (1978) described "hot DOP" aerosol size distributions produced by the ATI Q-127 machine more than a decade ago, and gave a good description of changes in aerosol GMD as indicated by readings of the mechanical analyzer (modified nephelometer) or "Owl" that is standard equipment on all Q-127s and TDA-100s. They found that the output aerosol could be varied over the GMD range $0.23\text{--}0.30 \mu\text{m}$, corresponding to changes in the angular reading of the Owl from 29° to 45° , respectively. These results can be compared to ours, which are reported below.

A model LAS-X laser aerosol spectrometer (Particle Measuring Systems, Inc., Boulder, Col.) was used in our research to measure GMD of test aerosols in four diameter ranges between 0.09 and $7.5 \mu\text{m}$. Fifteen channels of size resolution were provided in each range. Hinds et al. (1978) used a Particle Measuring Systems model ASASP-300 aerosol spectrometer; Skaats (1978) performed similar DOP studies using an LAS-200 laser aerosol spectrometer in tests to Army specifications with Q-127, Q-107, and Q-76 machines. We used precision gas diluters to prepare samples for size measurement from the Q-127, which were drawn from the analyzer (Owl) chamber, for introduction directly into the LAS-X system as described below.

SELECTION OF CANDIDATE MATERIALS

Toxicological properties of candidate materials were of paramount importance in our study. Classes or families of materials known to be noncarcinogenic and relatively non-toxic were required to be screened for possi-

ble candidates which, at the same time, had physical properties such that they might produce acceptable aerosols in the Q-127 machine. And, ideally, they should offer other inducements to their use such as low cost. Other factors that were considered in choosing materials to replace DOP were: 1) the impact of a new material upon existing testing hardware must be minimal; 2) machine maintenance—it is undesirable to use a material that will clog the testers and/or will support fungus growth; 3) destructive vs. nondestructive testing—DOP penetration testing is considered to be nondestructive, and a new material must also be nondestructive in the sense that it will not damage filters in standard test aerosol concentrations (even DOP might damage filters in massive concentrations); 4) a new material must exhibit adequate stability and aging characteristics, especially at elevated reservoir temperatures found in Q-127 machines.

Material Safety Data Sheets (MSDS) were compiled for promising materials, which included straight-chain saturated hydrocarbons (cosanes), moderately branched-chain saturated hydrocarbons, fatty acids, fatty acid esters, and glycols. The MSDS indicated that virtually all of these materials were classed as having very low toxicity to humans. Many, in fact, were approved for use in foods and cosmetics. But virtually no data were found to exist concerning the inhalation toxicity to humans of these materials when breathed as fine aerosols or smokes. Our approach was as follows: 1) find those materials that might work best in the Q-127 machine, considering a reproducible particle size, size distribution, smoke concentration, market availability, and cost; 2) subject those materials to replacement testing in production and/or product assurance penetrometer machines, and seek final approval for the use of any successful material(s) to replace DOP.

Many physical properties appear to play some role in the behavior of candidate materials when they are used in filter penetrom-

eter machines such as the Q-127. Among these physical properties are vapor pressure, surface tension, viscosity, and density.

Figure 3 presents a Clausius-Clapeyron plot for several potential candidate materials, relating the logarithm of vapor pressure to the reciprocal of absolute temperature in degrees Kelvin. The upper scale on the abscissa also gives temperature in degrees Celsius. The negative slope of the curve for each material corresponds to its heat of vaporization divided by the gas constant. Such curves are readily constructed if vapor pressures for a given material are known at two or more temperatures.

In Figure 3, it can be seen that the curve for DOP lies below the others, indicating that DOP has a lower vapor pressure at a given temperature than the other materials shown. As the molecular weight increases in a family of candidate chemical compounds, the vapor pressure decreases. Thus as the carbon chain length in capric, lauric, and myristic acids increases from $C = 10$ to 12 to 14, respectively, the curves in Figure 3 for these acids approach the lower curve for DOP.

This simple analysis suggests that as the fatty acid carbon chain length increases a better match is made with the vapor pressure characteristics of DOP. Thus palmitic acid ($C = 16$) or stearic acid ($C = 18$), which are not shown in Figure 3, should most closely match DOP in this respect. But the fatty acids just discussed are all solids at room temperature; their melting points range from 31°C for capric acid to 68°C for stearic acid. As their vapor pressure characteristics become more like those of DOP, they become increasingly difficult to work with. They will melt in the Q-127 machine pot and will vaporize, but the recondensation aerosols that they produce will become increasingly unpredictable with increasing chain length and melting point.

It is much easier to work with candidate materials that are liquids at room temperature. But such materials usually have two

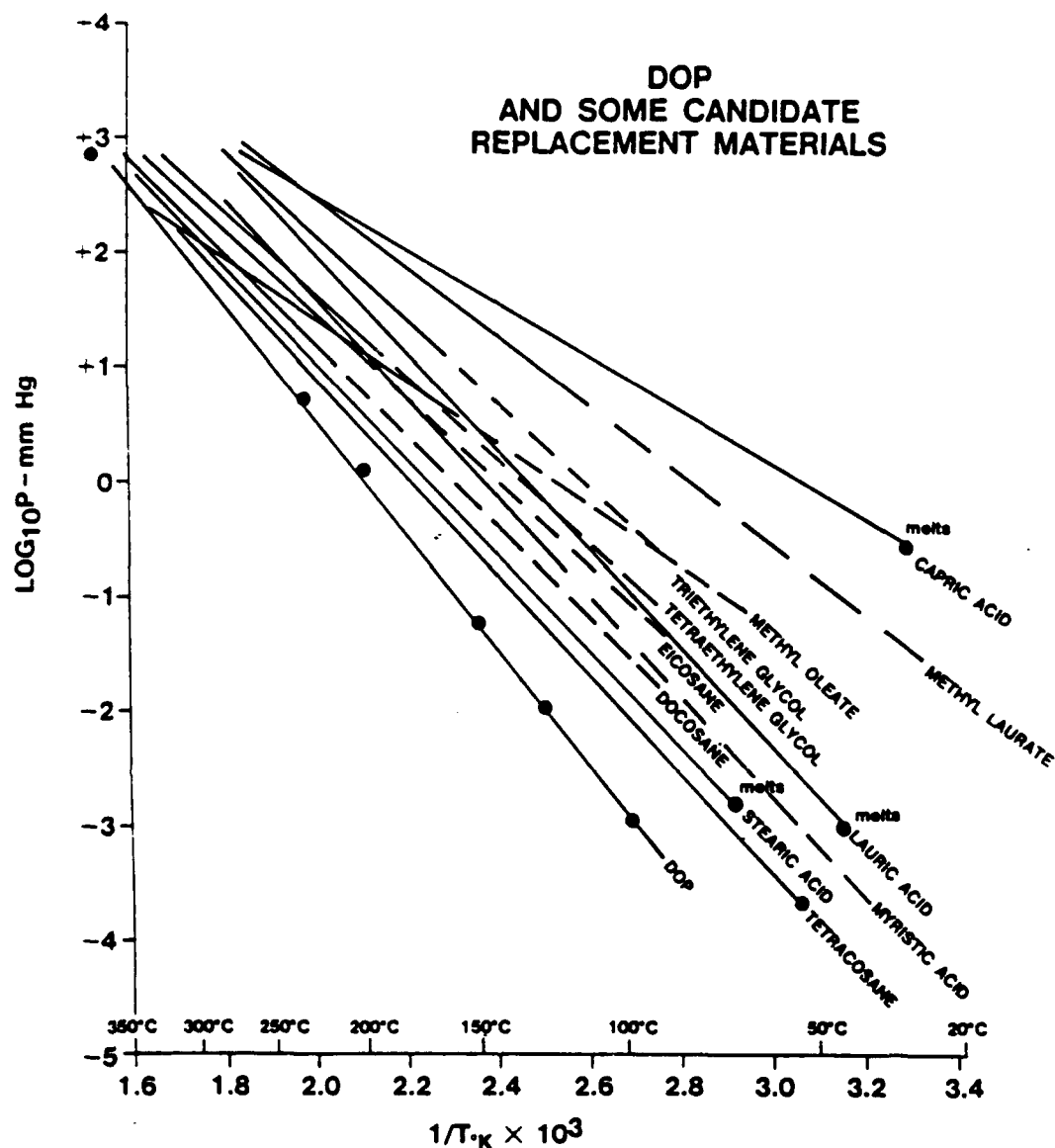


FIGURE 3. Clausius-Clapeyron plot: DOP and some candidate replacement materials.

characteristics that are undesirable: 1) they are unsaturated; i.e., they contain C:C double bonds that are sites for chemical attack leading to instability with aging, especially at elevated temperatures, and thus rancidity and fungus growth could result; 2) their carbon chains are branched, rather than straight as for the fatty acids just discussed,

and this increasingly complex structure increases the probability that human toxicological problems will be encountered in their use.

This analysis leads to the understanding that the search for materials to replace DOP must involve many compromises; indeed this is usually the case when replacements are

sought to be used in place of potentially hazardous materials so that testing can be carried out safely.

Figure 3 suggests how compromises might be made to find a simulant for DOP to use in the Q-127 machine. Suppose, for example, that the Q-127 machine pot is normally maintained at 150°C (shown on the upper abscissa scale in Figure 3) when it contains DOP. This corresponds to an ordinate value of -1.3, or a DOP vapor pressure of 0.050 mm Hg. Moving horizontally to the right at the -1.3 ordinate value, we encounter the myristic acid curve at a temperature of about 100°C. This indicates that we should obtain the same vapor pressure with myristic acid at a pot temperature of about 100°C that we would obtain with DOP at 150°C.

There are other complications. For example, the Q-127 machine pot temperature might not be conveniently adjusted to a temperature as low as 100°C. Even if this were possible, the acid might not recondense into an aerosol under conditions achievable using other Q-127 machine settings, or it might not yield an aerosol with the proper specifications. Even if the acid were to perform well, it would still freeze during shut-down in the Q-127 machine pot and fittings, because its melting point is 52°C. Its inhalation toxicological properties would still remain to be investigated. On the basis of all such considerations, we selected materials including those in Table 1 for investigation.

EXPERIMENTAL PROCEDURE

Our refurbished Q-127 penetrometer machine was supplied by air from a compressor. The inlet air line was fitted with a refrigerative dehumidifier to remove moisture and other contamination, such as oil, from the air supply.

The Q-127 machine was provided with precision capillary air diluters (TSI, Inc., St. Paul, Minn.) to sample aerosols for analysis by the LAS-X laser aerosol spectrometer (Particle Measuring Systems, Inc.). The air diluters were calibrated for dilution ra-

tios of 100:1 and 20:1 at maximum flow rates of 5 standard L/min. Each diluter employed a closed system using filtered air from the original sample to mix with and reduce the concentration of the aerosol at the output. The dilution air passed through two in-line HEPA filters. LAS-X data for the Q-127 machine were compared directly with those from the mechanical Owl on the Q-127 machine which was set to a given angular reading (usually 29°) to obtain a DOP aerosol having a given GMD. In this way, Q-127 machine operators could be instructed as to which control settings should be used to obtain proper test aerosols from DOP replacement materials, since they would not normally have access to a LAS-X system in filter quality testing.

A detailed Standing Operating Procedure (SOP) was prepared to permit safe machine operation with DOP, as well as with candidate replacement materials. Candidate samples were aged in an oven at 140°C concurrently with their use in the penetrometer machines. In this way the stability and aging characteristics of promising candidate materials could be studied over periods ranging from weeks to months, even though their time of use in the machines would be limited to days because of the pressing schedule of candidate material testing.

The Q-127 machine operating adjustments for particle size and distribution included pot temperature, quench air temperature, and vapor pickup air/quench air flow ratio. Some of these controls have been eliminated in the redesign of newer ATI model TDA-100 (formerly Q-127) machines. The test aerosol concentration is also directly proportional to the pot temperature. Quench air entering the system was maintained at 25°C by a heat exchanger connected to a circulating water chilling system. Quench air temperature was then regulated in-line by a heating element controlled by a Variac variable transformer on the control panel. The voltage setting corresponding to each air temperature was noted.

TABLE 1. Some Candidate Replacement Materials Investigated in This Study

Chemical family	Chemical name	Viscosity ^a or vapor pressure (mm Hg @ °C)	Specific gravity	Pour or melting point (°C)	Open cup flash Point (°C)
Cosanes	Mixed		0.80	-21	107
	Petroleum oils		0.81	-1	124
	<i>n</i> -hexadecane	< 1 @ 20	0.77	16	135
	<i>n</i> -octadecane	10 @ 174	0.77	28	165
	<i>n</i> -eicosane	14 @ 200	0.79	36	
	<i>n</i> -docosane	6 @ 200	0.79	44	
	<i>n</i> -tetracosane	3 @ 200	0.80	51	
Synthetic hydrocarbons	Poly-alpha olefins (PAOs)	2 cst viscosity ^a	0.80	-65	164
		4 cst viscosity ^a	0.82	-69	225
		6 cst viscosity ^a	0.83	-64	243
Fatty acids	Oleic acid	10 @ 224	0.89	11-14	193
	Isostearic acid	50 @ 265		12-15	182
	Stearic acid	10 @ 225		67	202
	Palmitic acid	100 @ 270	0.85	60	188
	Myristic acid	100 @ 251	0.85	52	177
	Lauric acid	100 @ 225	0.87	43	158
Fatty acid esters	Methyl oleate		0.87		163
	Methyl oleate stearate	10 @ 205		18	173
	Methyl stearate	10 @ 206		36	153
	Methyl palmitate	10 @ 184		27	165
	Methyl myristate	7 @ 156		19	
	Methyl laurate	10 @ 160		5	152
	Mixed fractions				
Polyethylene glycols (PEGs)	Tetraethylene glycol	14 @ 198	1.13	-6.2	
	Hexaethylene glycol				
Polyethylene glycol diesters					
Other materials	Erythritol				
	Pentaerythritol				
	Glyceryl stearate				

^aAt 100°C.

Vapor pickup and quench air flow rates were controlled by in-line flowmeters on the control panel. The ratio of quench air to vapor pickup air was shown to be optimum at 90:10 L/min, this ratio yielded the narrowest particle size distributions in most experiments. Given these flow rates, pot temperature and quench air temperature were the remaining particle size controlling parameters.

Candidate aerosols were initially generated at temperatures well below their flash points, usually at a pot temperature of 100°C. Mass concentration measurements were taken immediately, using preweighed filter papers in the test chuck. The Q-127 pot temperature was then adjusted to pro-

duce a target concentration of aerosol near 100 mg/m³, if achievable. Quench air temperature, for which the voltage was initially set at zero, was then increased until the target particle size was achieved.

If the particles were found to be too large with the initial control settings, the pot temperature was raised without approaching the flash point of the candidate material, so as to increase the pot/quench air temperature ratio. This effect also could have been produced by refrigerating the incoming quench air, but this would have necessitated a major machine modification and was not considered feasible.

Aerosol particle size and distribution were measured by diverting aerosol flow from the

Owl optical chamber through the capillary diluter system and into the LAS-X laser aerosol spectrometer. Sampling was done downstream of the optical chamber so as to permit simultaneous readings to be made using the Owl and LAS-X instruments.

When the desired particle size and nominal distribution were achieved, the LAS-X output was recorded and the Owl reading was recorded for reference in future operation of Q-127 machines for filter testing with DOP replacement materials, as discussed previously.

CANDIDATE MATERIALS TESTED

General

More than two dozen candidate materials were investigated as possible replacements for DOP in this research program (Table 1). The candidate materials that were tested were obtained either directly from primary manufacturers (see footnote to Table 2) or from secondary suppliers, whose unit prices ranged for five to ten times those of the manufacturers.

Available Toxicological Data

The toxicities to humans of all candidate materials that were tested were low according to MSDS provided by the primary manufacturers. For example, standard fatty acids and fatty acid esters are made from natural oils and are not required to carry warning labels, whereas the synthetic hydrocarbons (poly-alpha olefins [PAO]) have been FDA-approved for indirect food contact. But the word "unknown" appears on MSDS for inhalation toxicity for these and some other materials, in almost every case where the entry is not simply left blank. Generally, the cosanes are stated to be mild irritants, especially to sensitive skin, that can be decontaminated with soap and water and, if ingested, can be diluted with three to four glasses of water until the person affected

receives medical attention. Prolonged exposure is not recommended.

MSDS for all of the tested materials carried standard warnings against use of inadequate ventilation and uncontrolled environmental release, but no materials (except DOP and DOS) have been assigned occupational exposure limits including Occupational Safety and Health Administration (OSHA) PEL and/or ACGIH TLV.

For oleic acid, oleate esters, and isostearic acid, ingestion LD_{50} s of 20–50 mL/kg of body weight are typical in adult rats. Mild conjunctivitis of the eye and mild skin irritation, with slight erythema, are typical upon prolonged exposure to these materials.

The saturated straight-chain fatty acids and fatty acid esters have very low toxicities. LD_{50} s are in the range 10–20 g/kg or more, and eye and skin irritation are virtually nonexistent. The glycols also exhibit very low toxicities.

DOP: The "Standard" for Candidate Performance

The required performance criteria for candidate materials to successfully replace DOP are clear: they must be toxicologically and environmentally innocuous when dispersed as aerosols, and they must have physical and chemical properties sufficiently similar to those of DOP to allow them to produce aerosols like those of DOP when subjected to evaporation and recondensation in filter penetrometer testers like the Q-127 machine. Ideally, they should also work in machines that operate at room temperature. Table 3 gives Q-127 machine settings for typical operation with DOP, and ranges of GMD value, aerosol yield, and GSD (s_g) that result, for comparison with the candidate materials also shown there.

Selected Candidate Replacement Materials

Candidate materials as shown in Table 1 were obtained from several supplier including the primary manufacturers. These mate-

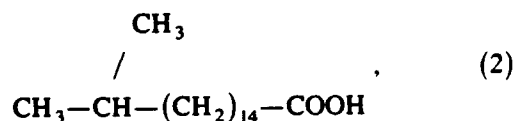
rials were either liquids or solids at room temperature. A test priority was established such that the materials were evaluated in the sequence: 1) liquids in the Q-127 machine; 2) solids in the Q-127 machine, in order of increasing melting point.

RESULTS AND DISCUSSION

Our experiments identified several materials that are viable candidates to replace DOP in hot smoke penetrometer machines such as Q-127. Table 2 summarizes the rankings of recommended replacement materials for DOP in Q-127 and TDA-100 machines, with sources of supply, and identifies the specific trade names and purities of the listed materials for comparison with the generic chemical names listed in Table 1. Emery 3004 is the 4 cst viscosity (at 100°C) PAO shown in Table 1, and Emery 3006 is the 6 cst PAO shown there. Additional data for specific material can be found in Table 3, for typical settings and performance specifications measured with our Q-127 machine using them. The materials identified here as DOP replacements are generally inexpensive, and readily available. Aging tests at elevated tempera-

tures, which are presently underway, should identify candidate materials that are thermally unstable. Most candidates should be quite stable in long-term testing, if not contaminated in use. Indeed, some candidate materials that contain significant percentages of "impurities" (compounds similar to the primary compound, but more volatile) actually seem to improve in performance with aging at elevated temperatures.

Isostearic acid has the structural formula:



where the single branched methyl group usually occurs in the position shown but also can occur at any other position along the carbon chain with a much lower probability. Thus it is an isomer of stearic acid, but the two acids have distinctly different physical properties. Isostearic acid is a light yellow liquid at room temperature.

Two samples of differing purity were used in this work. The purest sample was 70-76% isostearic acid, with the remainder consisting of myristic, isopalmitic, and palmitic

TABLE 2. Recommended Replacement Materials for DOP in Q-127 and TDA-100 Machines, Ranked in Order of Probable Success

Ranking ^a	Chemical name	Manufacturer or source
1	Synthetic hydrocarbon Emery 3004	Emery Group, Henkel Corp.
2	Isostearic acid (76%) Emersol 875	Emery Group, Henkel Corp.
3	Isostearic acid (66%) Emersol 871	Emery Group, Henkel Corp.
4	Synthetic hydrocarbon Emery 3006	Emery Group, Henkel Corp.
5	Oleic acid (71%) Industrene 206LP	Humko Chemical Div., Witco Chemical Corp.
6	Oleic acid (74%) Emersol 233LL	Emery Group, Henkel Corp.

Emery and Emersol products are available from Emery Group, Henkel Corp., Cincinnati, Ohio; Industrene products are available from Humko Chemical Division, Witco Chemical Corp., Memphis, Tenn.

^aHighest rankings have highest probability of success.

TABLE 3. CRDEC Q-127 Machine Settings to Produce DOP Replacement Aerosols, Showing Candidate Materials Ranked in Order of Probable Success^a

Ranking ^a	Material trade name	Typical performance		Owl Readings for Range of GMD (degrees)	Pot Temperature (°C)	Particle size control (voltage)	Ratio quench/vapor air	Footnotes ^b
		Range of GMD (μm)	Yield (mg/m ³)					
1	Emery 3004	0.20-0.30	70	1.23	170	46	90/10	A
2	Emersol 875	0.20-0.30	100	1.23	180	75	90/10	B
3	Emersol 871	0.20-0.30	76	1.20-1.25	155	69	90/10	C
4	Emery 3006	0.20-0.30	76	1.20-1.22	155	75	90/10	D
5	Industrene 2061LP	0.19-0.21	85	1.20	155	64	90/10	E
6	Emersol 233LL	0.18-0.30	110	1.20	155	70	90/10	F
		0.19-0.30	110	1.29-1.31	195	87	90/10	
		0.19-0.30	200	1.20	170	79	90/10	
		0.19-0.30	66	1.29-1.40 +	160	75	90/10	
		0.19-0.30	76	1.25-1.40 +	160	72	90/10	
		0.19-0.30	76	0.20 CMD	160	82	90/10	
For Comparison:								
	DOP	0.19-0.20	146	1.21-1.22	172	38	80/20	G
		0.25	146	29	172	38	80/20	
			146	48	172	100	80/20	
			146	48	172	100	80/20	

Test conditions: (a) Quench air held at 25°C before heating; (b) Line vacuum 5" mercury; (c) Air flow rates: through test chuck 32 L/min; through Owl 5 L/min.

^aHighest rankings have highest probability of success.

^bFootnotes: (A) synthetic hydrocarbon (see Table 2) Emery Group, Henkel Corp.; (B) isostearic acid, 70-76% pure, Emery Group, Henkel Corp.; (C) isostearic acid, 60-66% pure, Emery Group, Henkel Corp.; (D) synthetic hydrocarbon (PAO, see Tables 1 and 2) Emery Group, Henkel Corp.; 0.21 μm was maximum GMD attainable; (E) oleic acid, 71%, Humko Chem. Div., Witco Corp.; (F) oleic acid, 74%, Emery Group, Henkel Corp.; (G) the "standard" for candidate performance.

acids, in that order. The less pure sample was 60–66% isostearic acid, with the remainder consisting of isooleic, oleic, stearic, and isopalmitic acids, in that order.

Both samples worked very well in our Q-127 machine, with the purer material yielding slightly higher aerosol concentration. This can be observed in Table 3, with reference to Table 2. The oxidation stability of isostearic acid appears to be excellent compared to other candidate materials. A standard sample required 100 days to absorb 10 mL of oxygen at 60°C, while under the same conditions commercial oleic acid required only 1–7 days and glyceryl trioleate required only 5 hours. But, being a very weak acid, isostearic acid is not recommended for use in contact with chemically active metals such as copper and iron, especially at elevated temperatures. Stainless steel, or other inert materials, should be specified for the fabrication of the "hot pot," e.g., on TDA-100 machines, if isostearic acid is to be used owing to its other desirable properties.

Synthetic hydrocarbons include PAOs, which are used as synthetic lubricants, and in other applications. These versatile, saturated, synthetic hydrocarbons are produced by direct oligomerization of decene-1. Linear alpha olefins are polymerized and hydrogenated to manufacture PAOs. Three PAOs, were investigated in our studies; these are designated Emery 3002, 3004, and 3006. Data are summarized in Tables 1–3.

In our Q-127 machine, Emery 3004 performed best, giving a GMD adjustable from 0.2 to 0.3 μm , with a GSD of 1.23 and an adequate aerosol yield. The pot temperature was 180°C. Emery 3002 was too volatile, and produced large aerosol yields that could not be adjusted to GMDs below 0.3 μm , and which had GSD values of 1.40–1.67 or more. Emery 3006 had to be heated to 195°C to yield 110 mg/m^3 of aerosol with a GSD

value of 1.20, but the GMD could not be adjusted above 0.21 μm .

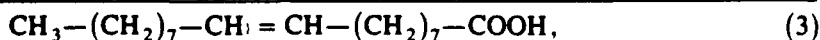
Oleic acid has the structural formula shown by Eq. 3, below, where one double bond exists between the ninth and tenth carbons of an 18-carbon chain. The molecule is most easily chemically attacked at this double bond, making this acid less stable during aging at elevated temperatures than saturated fatty acids. Nevertheless, it performs well in the Q-127 machine with the exception that the aerosol concentration is so great that it is sometimes difficult to control.

The oleic acid used here was 71–74% pure, with the remainder consisting mainly of palmitoleic and linoleic acids, in that order. It is a light yellow liquid at room temperature, with a slight odor.

COLLABORATIVE TESTING WITH THE MANUFACTURER

We were invited by the management of Air Techniques, Inc. to carry out comparative testing of DOP and our two best candidate replacement materials in three brand-new TDA-100 (formerly Q-127) penetrometer machines on their production line, during "break-in" in the early months of 1990. Data obtained from these tests were extremely valuable.

The materials selected for comparison with DOP were Emersol 875 isostearic acid, and Emery 3004 synthetic hydrocarbon (PAO). The reservoir (hot pot) of each machine was filled with one of the three materials. The machines were adjusted to give smoke yields at the test chucks of 100 mg/m^3 , in accordance with Army specifications. The DOP machine was adjusted according to ATI specifications for new machines, and the machines containing isostearic acid and PAO were initially set up using the control settings shown in Table 3, which were then modified to the extent



needed to obtain the required smoke yields. The machines, which were identical, were then operated for 100 hours on eight-hour daily, 40-hour weekly, schedules. Samples of the materials were collected into glass vials from the hot pots after approximately every 20 hours of operation, for future chemical analyses to determine whether decomposition, polymerization, or other changes occurred during this thermal "aging."

DOP and PAO were observed to have similar aging properties. Both remained clear for 10–20 hours of operation at temperature, and then exhibited a deepening honey color which turned to yellowish-brown after 100 hours. The isostearic acid, however, began to chemically attack brass parts used in the ATI machine hot pots. Within a few hours the liquid had turned greenish, and within 10–20 hours a deep greenish-black color developed. At the end of 100 hours, the material was black and quite viscous, indicating that polymerization might have been catalyzed by iron and copper complexes that were taken into solution. ATI engineers expressed an interest in experimenting with modified hot pots of stainless steel, glass, ceramic, or other inert construction, that should eliminate these corrosion problems. Such machine modifications might also reduce discoloration and sludging of DOP and other liquids used in the pots, thus increasing elapsed times to the accumulation of sludge, with required periodic maintenance, and requiring less frequent replacement of the material itself.

After the break-in period, our LAS-X and diluter systems were taken to the ATI factory for detailed measurements of the test smokes from the three machines. Trials were first run with the aged materials in the machines. The hot pots were then drained and refilled with fresh materials, and a second set of trials was run. The results with the aged materials showed that after 100 hours of operation the performance of the isostearic acid had improved somewhat, i.e., the GSD of the smoke which it produced had become

slightly smaller, whereas the GSDs of the PAO and the DOP had increased slightly. All three machines produced smokes with GMDs near $0.2\ \mu\text{m}$, and GSDs near 1.30. By changing the available adjustments of the machines (Figure 1), the GSDs of the isostearic acid and PAO smokes could be made to range from slightly above to slightly below a value of 1.30. Since the vapor pickup air temperature could not be controlled on these new-production TDA-100 machines (as it had been in the candidate studies with our older Q-127 machine), only a limited range of adjustment was possible to bring the smokes produced with our new materials to within Army specifications. The new TDA-100 machines are designed around standard DOP specifications, and their vapor pickup air operating temperatures are controlled by fixed-wattage heaters. Nevertheless, it was demonstrated that Army test specifications could be met with the new materials, without modification of the machines. ATI engineers indicated that if it were desired to deliver a new machine with, e.g., PAO instead of DOP, only a minor modification would be required to match the heater wattage to the proper operating temperature range of the replacement material, thus further improving the "monodispersity" of the test smoke.

After the machines were refilled with fresh materials, it was found that the specifications of the DOP and PAO smokes were very similar. Within the range of operating controls, the PAO smoke produced had a GMD of $0.22\ \mu\text{m}$ with a GSD of 1.29, while the DOP smoke, with optimum machine settings, had a GMD of $0.21\ \mu\text{m}$ with a GSD of 1.29. The fresh isostearic acid also was found to be able to produce a smoke that met Army specifications, within the available range of machine operating controls. But the latter material was not subjected to further detailed testing since, primarily because of its non corrosiveness and better aging properties, PAO was selected as the tentative candidate of choice to replace DOP in existing Q-127 and new

TDA-100 penetrometer machines with a minimum of downtime and machine modification. Further collaborative ATI/CRDEC tests are continuing, and results will be reported subsequently as detailed information becomes available concerning the direct replacement of DOP with PAO in these machines.

TOXICITY ASSESSMENT OF PAOS

Very recently manufacturers of PAOs including Emery 3004 have reissued MSDS, as required by law when previously unknown but pertinent information becomes available, to reflect the findings of Guiney (1982) on the acute toxicity assessment of PAOs.

The new Emery MSDS for PAOs claim that, although the toxicities estimated in Guiney's study were significant, the test conditions were such that the test animals (rats) were subjected to great physical insults, sufficient that observed histopathical changes may have been a response to these insults rather than being related to a specific compound toxicity effect. The MSDS contend that PAOs may be considered nonhazardous, for all practical purposes, by inhalation. Indeed all oils, including the purest of mineral oils, are capable of causing "oil pneumonia" and/or death by suffocation when inhaled at very high aerosol concentrations for periods of more than several minutes. Since oils cannot be cleansed easily from the lungs due to their extreme hydrophobicity, a buildup and coating of the lung surfaces is inevitable.

In summary, it would appear that the test conditions under which PAOs were considered to be potentially toxic by inhalation were decidedly unlike those reasonably expected to be found in actual experience. The acute toxicities of the PAOs are comparable to that of DOP. Since Emery 3004 is not toxic under normal operating conditions, and can replace DOP directly in operating machines (with no mission interruption and

while meeting or exceeding accepted Army filter test standards), it must be considered a prime candidate to be evaluated for approval as a DOP replacement by the U.S. Army Surgeon General. Procedures to request this approval are expected to be initiated during 1990.

CONCLUSIONS AND RECOMMENDATIONS

The replacement materials for DOP that are summarized in Table 2 can be expected to perform well in hot pot machines including the Q-127/TDA-100, and can also be considered for cold smoke applications where a less viscous, more volatile synthetic hydrocarbon (Emery 3002 PAO) probably would outperform Emery 3004. The PAO Emery 3004 is now the Army's primary candidate to replace DOP in hot smoke machines, including the Q-127 and TDA-100, primarily because of its ability to meet U.S. Army test specifications, its noncorrosiveness, its aging properties and cost which are similar to those of DOP, and its ability to be introduced into existing test machines in place of DOP with a minimum of mission interruption or need for machine modifications. These conclusions are, of course, subject to continued testing and refinement of data using various hot smoke machines, and to confirmation by chemical analyses of aging samples that potentially toxic or troublesome decomposition products (worse than those in DOP) are not found in replacement materials after prolonged use. It is concluded that isostearic acid also is a viable replacement material for DOP in hot (and probably cold) smoke machines, and that it might have advantages in some applications where, due to its molecular structure, it can be degraded by moisture whereas PAOs and other oily materials, including DOP, cannot be. Oleic acid also is worthy of consideration in some applications, although its unsaturated molecular structure renders it more susceptible to chemical breakdown and formation of by-products than the other replacement materials discussed here.

It is recommended that agencies engaged in systematic filter and respirator penetration studies employing testing machines using DOP should consider the use of Emery 3004 or isostearic acid in one or more of their machines, on a trial basis. If isostearic acid is used, it is recommended that modifications to machine hot pots be made to insure that only chemically inert surfaces, such as stainless steel or glass, can come in contact with this material. Machines should be adjusted, within available control ranges, to optimize test smoke specifications; these can be verified through the temporary use of laser aerosol spectrometers and air diluters as discussed in this paper.

It is also recommended that the replacement materials identified here should be considered for use in cold smoke machines which use spray-generated aerosols having broad particle size distributions. Problems such as rancidity often arise when, e.g., corn oil is used. The materials discussed here, and the polyethylene glycols (PEGs) (Gerber, 1980), represent viable alternatives for these applications.

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