# DOP SUBSTITUTES FOR QUANTITATIVE FIT TESTING: AEROSOL GENERATION AND DETECTION

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Substitutes for the test agent diethyl(hexyl)phthalate (117817) (DOP) used in respirator quantitative fit testing were investigated. Recent medical evidence has implicated DOP in the causation of liver cancer in test animals. Several model fluids with physical properties similar to those of DOP were examined. They were: diethyl(hexyl)sebacate (122623), linoleic-acid (60333), oleic-acid (112801), dimethicone (9006659), and corn-oil. The fit test apparatus generated aerosols from these fluids and chemical properties were observed. The fit test apparatus was capable of producing the required quantities of aerosol from all the fluids tested. Mass median diameters and geometric standard deviations of the aerosols were all comparable. The required protection factor could be measured with the aerosols produced from any of the oils tested. The authors note that oils with physical properties similar to those of DOP are potential candidate materials for use in quantitative fit testing.

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# ABSTRACT

In response to recent data developed by the National Cancer Institute indicate that di-ethyl(hexyl)phthalate [commonly called di-octyl phthalate (DOP)] may be a carcinogen, NIOSH promptly began a study to find a replacement for DOP used in quantitative fit testing of respirators. The study selected several model fluids having physical properties similar to those of DOP. The fit test apparatus was able to generate aerosols of each of the fluids at a concentration similar to that of DOP. The aerosol characteristics of mass medium diameter and geometric standard deviations were also similar to those of DOP. Some chemical properties which may affect the stability of the fluids were observed and recommendations noted. Therefore, by selecting fluids with physical properties similar to those of DOP, there are a number of candidate materials for use in quantitative fit testing of respirators. The determination of the most suitable material in terms of toxicological properties remains to be completed.

## I. Background and Introduction

Use of respiratory protective devices has been dated to the first century where loose fitting animal bladders were used to protect miners from the red oxide of lead.(1) Development of respiratory protective devices was slow until the 1800's, when the discovery of Brownian motion led to a better understanding of the mechanisms of filtration and subsequently to better respirators. During this same period, the discovery of the adsorptive properties of activated charcoal also contributed to rapid advances in respiratory protection.

Today respirator technology has reached a point where the respirator-to-face sealing surface is a major source of potential leaks and wearer exposure to toxic chemical agents. Various procedures have been developed to test respirator fit, both qualitatively and quantitatively.(2a-i) Qualitative fit tests require subjective wearer response to leakage of a test agent into the respirator. The particular response (e.g. odor, irritation, etc.) varies among individual wearers, and, thus, the test can be variable and arbitrary.(3) With quantitative fit testing, the fit test equipment challenges the respirator with a known concentration of chemical agent and measures the leakage of test agent into the wearer's respirator. Using this measurement, an actual degree of fit or protection factor can be calculated. By utilizing facial anthropometric data and quantitative fit test results, protection factors have been assigned to certain types of respirators (e.g. half masks, full facepiece, etc).(4a-b) These assigned protection factors refer to the minimum protection offered, in terms of a multiple of permissible exposure levels (e.g. 10 X PEL, 1000 X PEL), for that type of respirator. Presently, quantitative fit testing is used to ensure that an individual wearer has obtained at least this minimum assigned protection factor when using a particular respirator type.

The majority of respirator fit test equipment in use today utilizes either a polydisperse sodium chloride aerosol or a polydisperse "dioctyl" phthalate (DOP, also known as di(2-ethylhexyl) phthalate) challenge aerosol. Each type of aerosol has its advantages in different situations. The sodium chloride systems are applicable when testing the fit of respirators with small assigned protection factors (protection factors of 10 to 50), such as negative pressure air-purifying respirators. "Dioctyl" phthalate-based systems using light scattering aerosol detectors are more sensitive to detecting small leaks and are preferred for fit testing respirators with higher assigned protection factors (e.g., self-contained positive pressure breathing apparatus, with a protection factor ∿10,000). Ease of aerosol detection and aerosol generation have made dioctyl phthylate respirator fit apparatus popular in many industrial respirator fit test program.

Recent evidence on DOP from the National Cancer Institute has tentatively implicated this compound in the causation of liver neoplasms in both rats and mice. This information raises concern over the continued use of DOP as a test agent in respirator quantitative fit testing. Since the fit testing of respirators with large protection factors relies on methods using DOP, substitution of a less toxic material for DOP is essential.

## II. Experimental

Selection of a substitute material involved consideration of several physical and chemical properties, such as melting and boiling points, density, surface tension, vapor pressure, viscosity, refractive index, flash point, and explosive limit. In addition, the ease of cleanup, odor, and color were considered. Likewise, existing toxicological data on candidate materials were a major consideration in the selection process. A number of fatty acid oils were in use in several aerosol research laboratories throughout the U.S. Although pure chemicals would result in better control over physical, chemical and toxicological properties, natural and synthetic mixtures were also evaluated on recommendation by the fit test equipment manufacturers.

The di(2-ethylhexyl) phthalate (DOP) and di(2-ethylhexyl) sebacate (DOS) were chromatographic grade and were obtained from Analabs, Inc. The linoleic acid was purified grade and was obtained from Fisher Scientific Company. The corn oil used was Mazola 100% Pure Corn Oil and was obtained at a local grocery store. The dimethicone silicone oil was Dow Corning 200 fluid (50 c.s.) and was obtained from Dow Corning Corporation. Table I gives a list of the physical properties of these materials.

The experimental protocol was aimed at finding a suitable fluid which could replace DOP in respirator quantitative fit test procedures. This meant that the challenge aerosol output of an existing DOP respirator fit test apparatus had to be measured for concentration, aerosol mass median diameter and geometric standard deviation. Also the photometer detector had to be checked for sensitivity to these aerosols.

The aerosols were generated from the various oils using a model TDA-50 DOP Man Test Penetrometer (Air Techniques Incorporated, Baltimore, Maryland). The TDA-50 employed a Laskin type nebulizer with either a 2-jet or a 4-jet nozzle(6) and supplied both the generator air and dilution air. Early models of the TDA-50 were supplied with a 4-jet nebulizer. In recent versions, two of the jets were blocked off to produce a lower challenge aerosol concentration. The aerosol was mixed with dilution air in a baffled mixing chamber. The TDA-50 also employed a forward scattering photometer for measuring both the challenge aerosol and the aerosol in the respirator mask. The photometer display covered the ranges 0-100%, 0-10% and 0-.1% full scale. After the aerosol was generated and diluted to the desired concentration using the TDA-50, it passed into a test chamber (16" diameter and 28" long) in which concentration and size distribution of the aerosol were measured (Figure 1).

The mass concentration of the aerosol was measured by collection on 4" Gelman Type A glass fiber filters held in Sierra model 710 filter holders. The filters were weighed to ± 10 μg on an analytical balance before and after the aerosol was collected. The size distribution of the aerosol was measured using an Electrical Aerosol Analyzer (EAA)(Thermo Systems model 3030) and an active scattering aerosol spectrometer (Particle Measuring Systems, Inc., model ASAS-X). The aerosol from the measuring chamber was diluted using a Royco 252 dilutor to prevent saturation of detectors in the ASAS-X and EAA. The data from the EAA were analyzed using the monodisperse calibration constants supplied in the user manual. The Royco 252 dilutor was also used to check the various ranges on the TDA-50 photometer. Since the Royco 252 dilutor provided a nominal dilution ratio of 100/1, it was used to check the 0-1% range on the photometer. Two Royco 252 dilutors were also operated in series to provide a nominal dilution ratio of $10^4/1$ to check the 0-.1% range on the photometer.

An attempt was also made to measure the amount of gas phase DOP that was associated with the DOP aerosol. This was done by sampling the DOP aerosol onto a 4" glass fiber filter followed by two impingers in series. Each impinger contained 25 ml of isopropanol. The amount of DOP collected in each impinger was measured by the UV absorption of the DOP at 224 nm. The amount of DOP collected on the filter was measured by weight difference and by extraction of the filter with 80 ml of isopropanol and measurement of the extracted DOP by UV absorption at 224 nm.

A typical generation experiment was performed as follows. The generator and dilution air were turned on and adjusted to the proper pressures and flows according to the manufacturer's recommendation. Filter sampling for mass concentration measurement was begun after the concentration in the chamber had stabilized. At that time, the particle size distribution was measured using the EAA and ASAS-X. The TDA-50 photometer scale was set to 100% on the challenge aerosol. Then the photometer's response was measured for one stage and two stages of dilution with the Royco 252 dilutors.

## III. Results and Discussion

Table II gives the mass output of the generator for the various oils. DOP was tested using both the 2 jet and 4 jet nozzles, while the other oils were tested using only the 2 jet nozzle. It can be seen from Table II that all the oils produced similar aerosol mass concentrations.

Table III gives a summary of the particle size measurements made for the aerosols of the various oils. Also included in Table III is the photometer response for one stage of dilution and two stages of dilution using the Royco 252 dilutors. The final column of Table III gives volume concentration of the aerosol as measured by the EAA. This column was added to show that although dimethicone produced the same mass concentration of aerosol as the other oils, the volume concentration as measured with the EAA was considerably less than the other oils. This may be due to a loss of aerosol between the measuring chamber and the EAA caused by excessive charging of the aerosol. It can be seen from Table III that the aerosols produced from all mass median diameters and standard deviations. Also, the photometer appears to have sufficient sensitivity to measure protection factors of $10^4$ when used with any of the aerosols produced from the oils under the conditions tested.

The amount of gas phase DOP associated with the DOP aerosol was determined with the glass fiber filter followed by two impingers in series. The filter indicated a DOP concentration of 159.6 mg/$m^3$ while the first impinger indicated a concentration of 8.6 mg/$m^3$ and the second impinger gave a concentration of 3.1 mg/$m^3$.

Several phenomena were observed that may effect the long term stability of aerosol generation. Linoleic and oleic acids reacted with the brass fittings of the nebulizer. The linoleic acid turned yellow indicating oxidation of the molecular double bonds.

The corn oil had a cloudy appearance and exhibited a slight increase in viscosity after two days of aerosol generation. The cloudiness was probably due to entrapped water and air. An 8% increase in viscosity was measured with a Zahn viscometer. The changes did not affect the operation of the fit tester, but indicated that periodic changing of the oil may be necessary.

## IV. Conclusion

The fit test apparatus is capable of producing the required quantities of aerosol from all the fluids tested, including DOP. The mass median diameters and geometric standard deviations of the aerosols are all comparable. The required protection factor of $10^4$ can be measured with the aerosols produced from any of the oils tested. Apparently, any oil with similar physical properties is suitable in terms of the generation and detection system. Two factors affecting long term stability are noted: acids will attack the brass fittings of the nebulizer, and unsaturated hydrocarbon compounds will oxidize and become increasingly viscous. Replacement of the brass fittings with stainless steel or other inert fittings would eliminate any corrosion problems. Periodic replacement of the unsaturated hydrocarbon oils will prevent problems due to oxidation of the oil.

Thus by selecting oils with physical properties similar to those of DOP there are a number of candidate materials for use in quantitative fit testing. The determination of the most suitable material in terms of toxicological properties remains to be completed.

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## TABLE I

### PHYSICAL PROPERTIES OF DOP AND OTHER SUGGESTED COMPOUNDS FOR RESPIRATOR FIT TESTING

| | PHYSICAL STATE | M.P. (°C) | B.P. (°C) | DENSITY (SP. GRAVITY) (dyne/cm$^2$) | SURFACE TENSION | VAPOR PRESSURE (mm Hg) | REFRACTIVE INDEX | COLOR | FLASH POINT (°C) | EXPLOSION LIMIT (°C) | MOLECULAR WEIGHT | VISCOSITY (Centistrokes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Di-ethyl(hexyl)phthalate | liquid | -55[3] | 230 (5mm)[3] | (20°/20°C)[3]<br>.9861 | | 1.2 (200°C)[4]<br>$5\ 10^{-7}$ (25°C)[5] | 1.4836[4] | Colorless[3] | 220.6[3] | | 390.6[3] | 57.4 (25°C) |
| Di-ethyl(hexyl)sebacate | liquid | -55[4] | 248 (9mm)[3] | (25°/25°C)[3]<br>.913 | | | 1.447[4] | Colorless[3] | 215[3] | | 426[3] | 27.4 (25°C) |
| Linoleic acid (9,12 octadecadienoic acid) | liquid | -12[3] | 230 (16mm)[3] | (10°/40°C)[3]<br>.903 | | | 1.4699[1] | Colorless[4] | 188.9[7] | | 208.4[3] | 28 (38°C) |
| Oleic acid (9, octadecenoic) | liquid | -13.2[4] | 225 (10mm)[5] | (25°C)[3]<br>.895 | 32.5[1] | 1 (176°C)[3] | 1.4599[4] | (pure)[4]<br>Colorless | 188.9[3] | (auto ignite)[4]<br>362.8 | 282.4[3] | 28.6 (30°C) |
| Dimethicone (dimethyl polysiloxane) | liquid | -94[6] | 250[6] | 0.960[6] | 20.6[6] | | (25°C)[6]<br>1.401 | Colorless[6] | 285[6] | | | 50 (25°C) |
| Corn Oil | liquid | -20[1] | | (15°C)[1]<br>.922 | | | 1.4734[1] | Light Yellow | | | | |

## TABLE II

## GENERATOR MASS OUTPUT

| Oil Generator Pressure (psi) | Dilution Air (Lpm) | Mass Output ($mg/m^3$) |
|---|---|---|
| DOP (2 jet) 5 | 247 | 134.0 |
| DOP (4 jet) 5 | 247 | 195.0 |
| Dimethicone (2 jet) 5 | 247 | 121.0 |
| Corn Oil (2 jet) 5 | 247 | 118.1 |
| DOS (2 jet) 5 | 247 | 159.1 |

## TABLE III

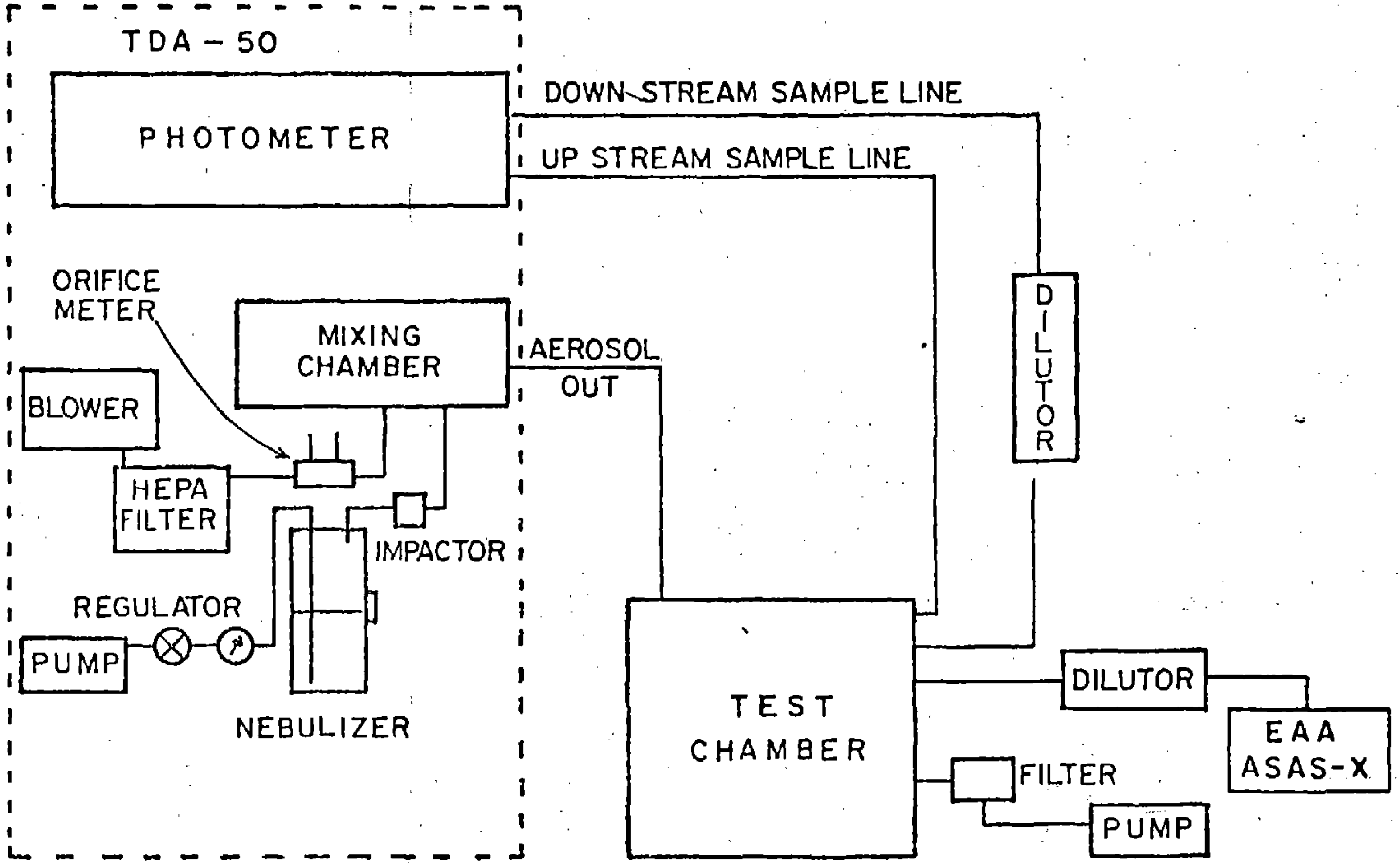
## PARTICLE SIZE PARAMETERS FOR OIL AEROSOLS

| Oil/Generator/Pressure (psi) | MMAD | σ g | 1-Stage Dilution | 2-Stage Dilution | Aerosol Volume Concentration ($\mu m^3$/cc) |
|---|---|---|---|---|---|
| DOP/4 jet/5 | .53 | 1.83 | 1% | .012% | $.341 \times 10^5$ |
| DOP/4 jet/3 | .53 | 1.83 | — | — | $.136 \times 10^5$ |
| Linoleic Acid/4 jet/5 | .56 | 1.96 | 1.2% | .012% | $.357 \times 10^5$ |
| Dimethicone/4 jet/5 | .57 | 1.84 | 1.3% | .013% | $.934 \times 10^4$ |
| Dimethicone/2 jet/5 | .57 | 1.84 | 0.8% | .011% | $.456 \times 10^4$ |
| Corn Oil/2 jet/5 | .53 | 1.85 | 1.0% | .015% | $.130 \times 10^5$ |
| DOS/2 jet/5 | .63 | 1.94 | .97% | .013% | $.169 \times 10^5$ |
| DOP/2jet/5 | .53 | 1.83 | .97% | .012% | $.169 \times 10^5$ |

* Linoleic acid caused oxidation of brass generator parts and the linoleic acid turned yellow after use.

* Corn oil appeared to get thicker and cloudy after use.

FIGURE I



Aerosol generation and test system.