

Decomposition of Dioctyl Phthalate (DOP)

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Abstract

A controlled study was conducted to quantify the changes in the purity, structure, and (aerosol) particle size distribution of dioctyl phthalate (DOP) after prolonged heating in a "hot smoke" DOP penetrometer.

Several instrumental techniques were employed to determine the purity, structure, absorption of visible light and particle size distribution of the fresh and exposed (336 hours at $167 \pm 2^\circ\text{C}$) DOP samples. These techniques included X-ray fluorescence, gas chromatography-mass spectrometry, Fourier Transform infrared analysis, UV-visible spectrometry and light scattering techniques.

Testing and analysis revealed that the DOP experiences very little decomposition (purity of 99.11% for fresh vs 98.49% for exposed) after prolonged heating (336 hours at $167 \pm 2^\circ\text{C}$) in the ATI DOP Penetrometer. Analysis also indicated that the exposed DOP's brown color is due to the presence of a trace quantity (a few tenths of a percent) of a high molecular weight hydrocarbon produced primarily by the reaction of the 2-ethyl hexanol impurity within the fresh DOP.

Finally, gas chromatograph and light scattering measurements revealed that insignificant differences exist between the purity and character (distribution of particle sizes, geometric mean diameter and standard deviation) of the aerosol particles generated from the fresh and exposed DOP samples.

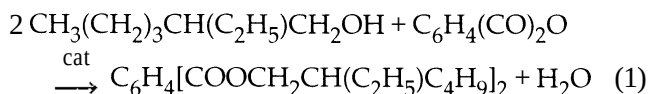
Introduction

Recently, concern has arisen that dioctyl phthalate (DOP) decomposes after prolonged use in the "hot smoke" DOP generator. MSA's Chemical R&D Group conducted a controlled study to demonstrate that DOP does not decompose after prolonged heating in the "hot smoke" penetrometer. Specifically,

the changes in the purity, structure, and aerosol particle size distribution of DOP after prolonged heating in a penetrometer were determined. The details of this investigation and analysis of the results are presented in this report.

Materials and Sample Preparation

Diethyl phthalate (di[2-ethylhexyl] phthalate) is produced by the reaction of 2-ethyl hexanol and phthalic anhydride. See Equation 1. Although the reaction is usually catalyzed by tetrabutyl titanate; toluene sulfonic acid *and* dibutyl tin oxides have also been used. Diethyl phthalate is commercially available in purities of at least 96%. Several important properties of DOP are presented in Table I.



Diethyl phthalate (DOP) has the unique properties of a high boiling and flash point, and a low glass transition temperature. These properties have made it a popular plasticizer for vinyl resins where thermal stability (for extrusion or molding of resins at temperatures exceeding 200°C), and low temperature

flexibility (glass transition temperature < -20°C) are necessary.

The DOP used in this investigation was produced by the Celanese Corporation. Celanese stated that this grade of DOP has a purity of approximately 99%. The material was received and stored, until use, in a sealed 5 gallon metal drum at 25°C. The fresh DOP sample was taken directly from this drum. To prepare the exposed sample, 500 ml of DOP was taken from the drum and placed in an ATI Q127 DOP Penetrometer where it was heated for 42 eight-hour cycles (336 hours in total) at $167 \pm 2^\circ\text{C}$. No additional DOP was added to the penetrometer during this period. The penetrometer is normally operated at $167 \pm 2^\circ\text{C}$ to test sample filter efficiencies. At this temperature, enough DOP is volatilized to result in an airstream concentration of 100 micrograms of DOP per liter.

Instrumentation and Testing Procedures

All testing was performed at the MSA J. T. Ryan Research and Engineering Laboratory. Several instrumental techniques were employed to determine the purity, structure, absorption of visible light, and particle size distribution of the fresh and exposed DOP samples. These techniques included X-ray fluorescence, gas chromatography-mass spectrometry, Fourier Transform infrared analysis, UV-visible spectrometry, and light scattering techniques. All of the instruments were calibrated before use, and testing was performed in duplicate or triplicate.

A Spectrace Model 6000 X-ray fluorescence spectrometer was employed to determine the

presence of trace quantities of unreacted catalyst in the fresh DOP. A Hewlett Packard Model 5995 gas chromatograph-mass spectrometer equipped with a Supelco SP5, 15 meter, 530 micron column was used to quantify the purity, and identify organic impurities within the fresh and exposed DOP samples. One microliter samples of the fresh and exposed DOP were injected into the gas chromatograph operating at the following conditions:

Helium carrier gas flow rate = 20cc/minute
Injector temperature = 280°C
Oven temperature = 50°C to 320°C at a heating rate of 10°C/minute
Duration at 320°C = 23 minutes

Table I. Properties of dioctyl phthalate.

Available purity	96+%
Molecular Weight	390 grams/mole
Flash Point	218°C
Boiling Point	231°C
Vapor Pressure	1.32mm Hg @ 200°C
Specific Gravity	0.986
Glass Transition Temperature	< -20°C
Refractive Index	1.4836

To accurately quantify the purity of the DOP samples, the peak areas within the gas chromatograms were quantified (integrated) by Janel's Sigma Scan/Image Software-Version 1.2.

A Nicolet Magna 550 Fourier Transform Infrared Spectrophotometer equipped with an attenuated total reflectance accessory and zinc selenide crystal was employed to determine the differences between the chemical structures of the fresh and exposed DOP samples. A Spectronic Model 1000 UV-Visible spectrometer was used to determine the wavelengths of light absorbed by 10 ml samples of the fresh and exposed DOP.

A 500 ml sample of each of the fresh and the exposed DOP was placed into the ATI reservoir and heated for at least 30 minutes until a sample steady state temperature of $167 \pm 2^\circ\text{C}$ and a concentration of 100 micrograms of DOP per liter of smoke were reached. The smoke (aerosol) was routed through a Gelman Supor-100 micropore (0.1 micron pores) filter and a 150 mg carbon bed at an airflow rate of 1 liter per minute, for a period of four hours.

The DOP which had been collected was desorbed by placing the micropore filter and carbon bed

into separate glass vials which contained 3 ml of carbon disulfide. The glass vials were then sealed and placed into an ultrasonic bath for 30 minutes. Afterwards, one microliter samples were extracted from the vials and injected into the gas chromatograph-massspectrometer.

Finally, an ATI Q127 DOP Penetrometer interfaced to an ATEC Model 303 dilution unit and a Particle Measuring Systems Model LAS-X laser/aerosol spectrometer was used to count the aerosol particles generated from the fresh and exposed DOP samples. A 500 ml sample of each of the fresh and the exposed DOP was placed into the ATI reservoir and heated for at least 30 minutes until a sample steady state temperature of $167 \pm 2^\circ\text{C}$ and a concentration of 100 micrograms of DOP per liter of smoke were attained. The DOP aerosol was diluted with the ATEC dilution unit (operating at a flow rate of 5 cc/second) and subsequently introduced into the LAS-X spectrometer where the number of particles of specified sizes were counted. Three consecutive 20 second samplings were taken and averaged. Five minutes passed between each measurement.

Test Results

X-ray fluorescence revealed that little or no inorganic-based catalyst impurities are present in the fresh DOP. (Note: The lower detection limit for the XRF is 10 ppm by weight.) The gas chromatograms for the fresh and exposed DOP samples are presented in Figures 1 and 2, respectively. The purity of each sample was determined by ratioing the integrated area of the "parent" DOP peak (between retention times of approximately 16.75 and 45 minutes) to the total area of all of the peaks. The calculated purity of the fresh and exposed DOP samples are comparable to one another (99.11% for fresh vs 98.49% for exposed). See Table II. In addition to the "parent" DOP (di[2-ethylhexyl] phthalate) peak, the fresh sample has peaks at retention times of 7.78 and 9.92 minutes, while the exposed sample has a peak at 5.31 minutes and a "shoulder" near 16 minutes.

Mass spectrometry revealed that the peaks in the fresh DOP at 9.92 and 7.78 minutes are associated with a 2-ethyl hexyl benzoic acid ester and 2-ethyl hexanol, respectively. The very small impurity peak in the exposed sample at 5.31 minutes is associated

with phthalic anhydride. The "shoulder" near 16 minutes is associated with a long chain hydrocarbon.

The infrared analysis spectra for the fresh and exposed samples are presented in Figures 3 and 4. Overall, the spectra revealed that the fresh and exposed DOP samples contain the same functional groups. After normalization of the spectra off of the prominent carbonyl (C-O) stretch at 1271 cm^{-1} , most of the C-H and C-C stretches for the exposed sample are of greater intensity than those for the fresh sample. However, the C-O stretching for the exposed sample is slightly less intense than that for the fresh DOP. See Table III.

UV-visible scans in the wavelength range of 200 to 900 nm are presented in Figure 5. The fresh sample which is clear (refractive index of 1.4836 vs 1.33 for water) absorbs little or no radiation in the visible region (380 to 780 nm). Conversely, the exposed sample which is amber to dark brown in color absorbs radiation in the UV ($< 380\text{ nm}$) and visible regions up to wavelengths as great as 800 nm.

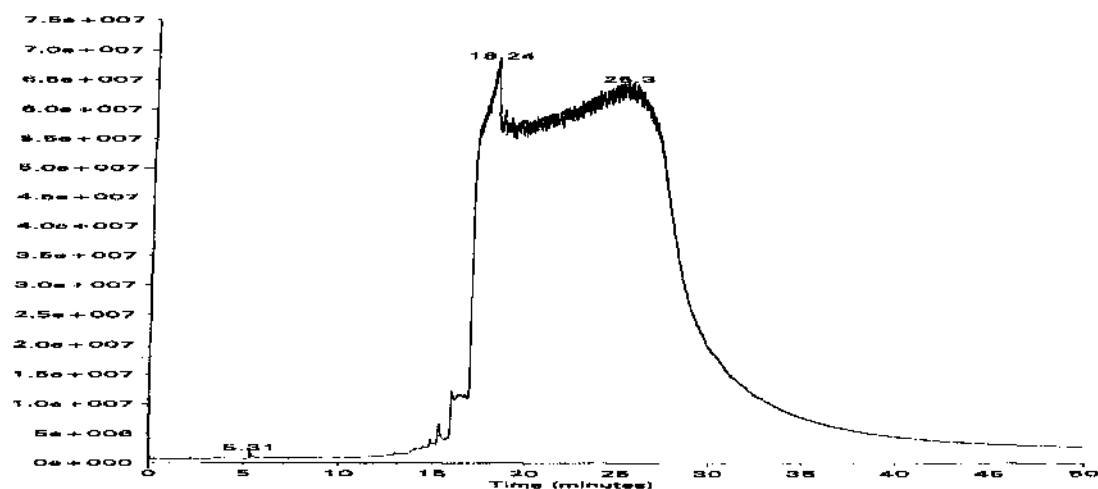


Figure 1. Gas chromatogram of fresh DOP from penetrometer reservoir.

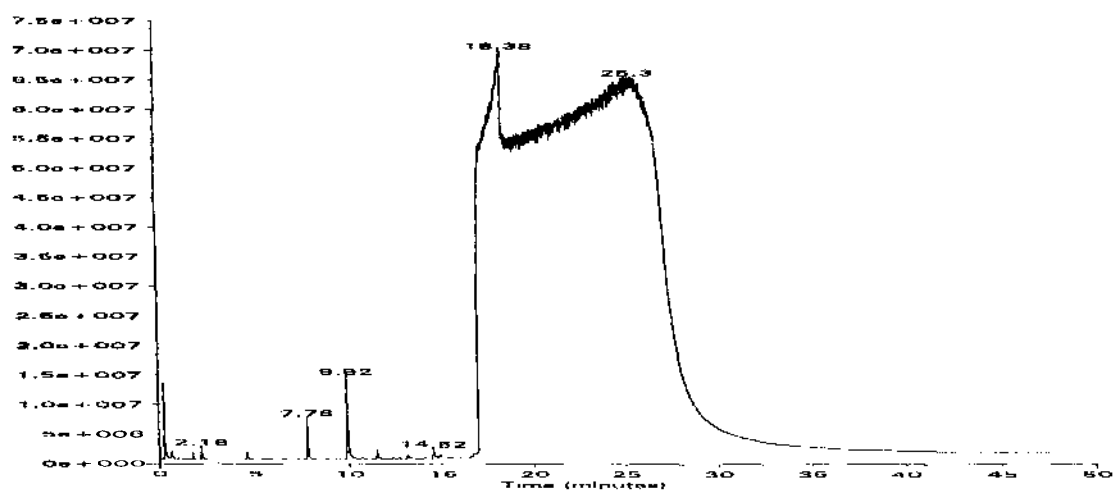


Figure 2. Gas chromatogram of aged DOP from penetrometer reservoir.

Table II. Gas chromatography peaks of fresh and exposed DOP.

Peak retention sample	Time, minutes	Count of integrated area	% of total area
Fresh DOP	16.75-45	356303	99.11
	7.78	614	0.17
	9.92	1259	0.35
Total of all other peaks	1325	0.37	
Exposed DOP	16.75-45	416985	98.49
	5.31	133	0.03
	16.00	6262	1.48

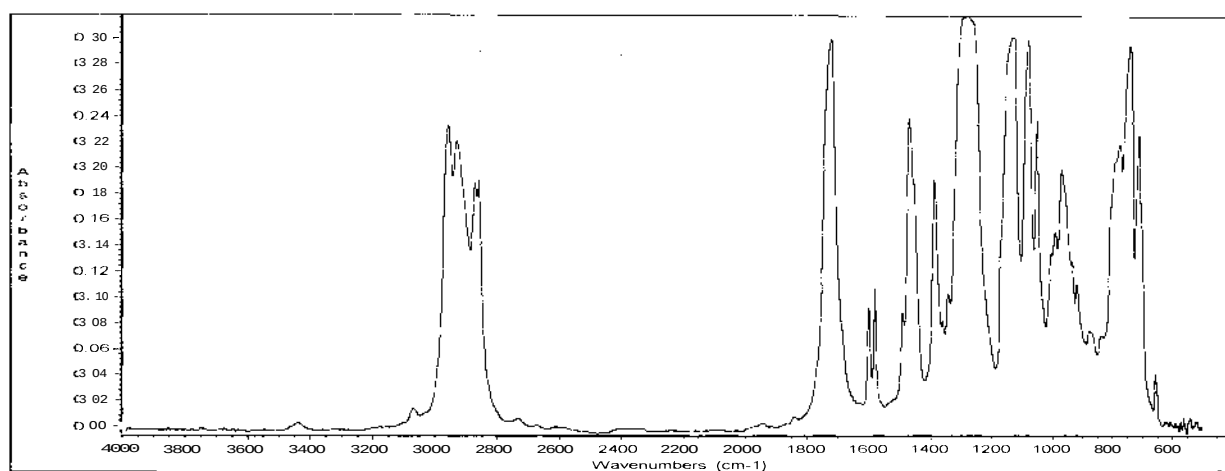


Figure 3. Infrared spectrum of fresh DOP.

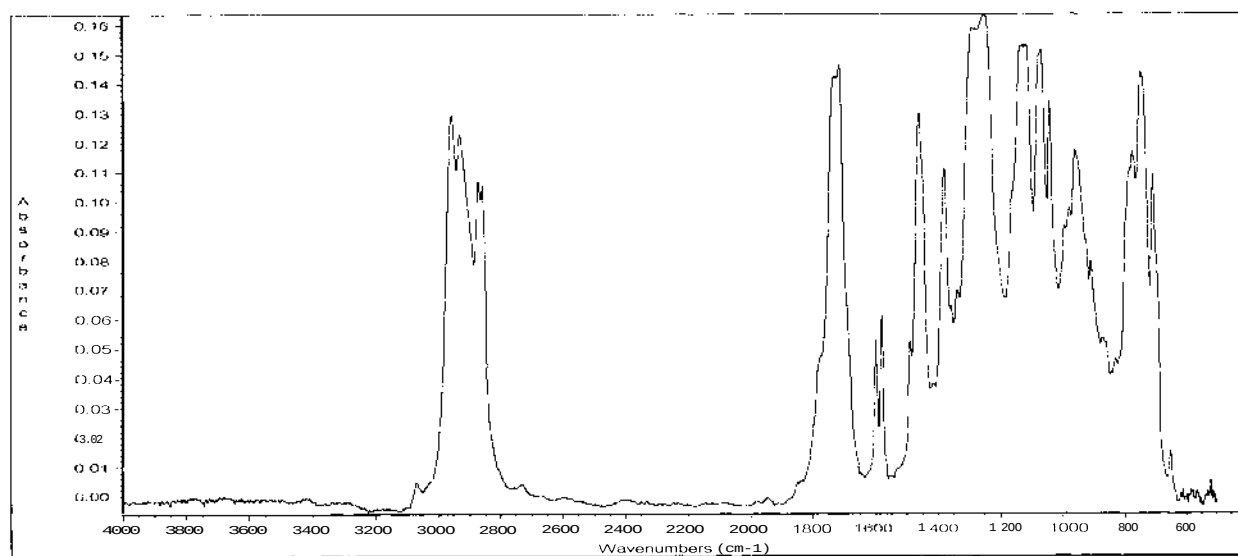


Figure 4. Infrared spectrum of exposed DOP.

Table III. Normalized infrared adsorption peaks of DOP samples.

Frequency CM^{-1}	Fresh DOP absorbance	Exposed DOP absorbance	Type of stretch
652	0.114	0.109	C-H
705	0.708	0.693	C-H
742	0.924	0.893	C-H
769	0.683	0.711	C-H
868	0.222	0.331	C-H
908	0.337	0.489	C-H
958	0.622	0.717	C-H
978	0.467	0.602	C-H
1040	0.843	0.819	C-O
1071	0.940	0.928	C-O
1118	0.949	0.940	C-O
1271	1.000	1.000	C-O
1338	0.317	0.344	C-O
1380	0.603	0.693	C-H
1462	0.756	0.807	C-H
1488	0.276	0.343	C-H
1580	0.343	0.398	C-C
1600	0.292	0.349	C-C
1719	0.949	0.916	C-O
2860	0.610	0.645	C-H
2873	0.603	0.651	C-H
2930	0.705	0.747	C-H
2958	0.740	0.783	C-H

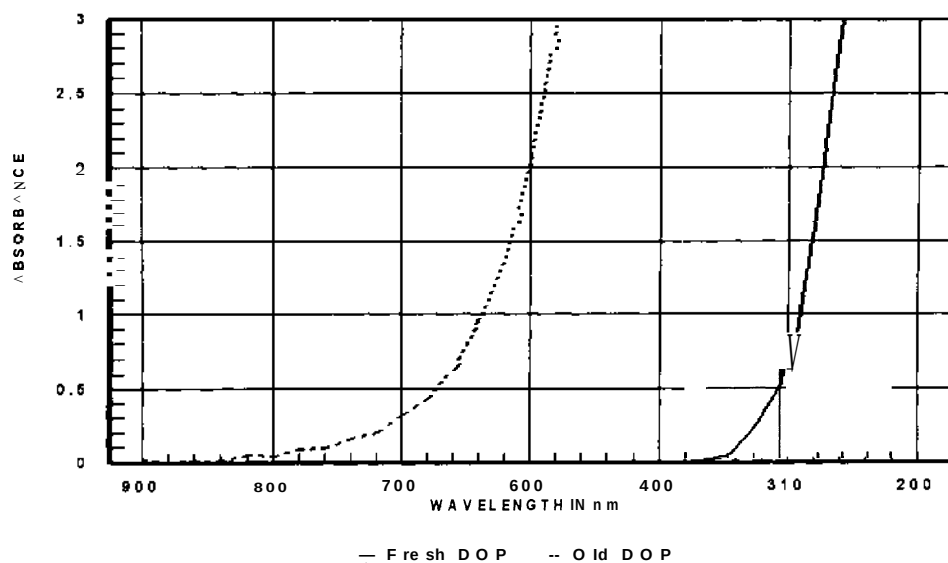


Figure 5. UV-visible adsorption spectrum of fresh and exposed DOP.

Gas chromatography-mass spectrometry revealed that the purities of the smoke generated from the fresh and exposed DOP (collected on the microporous filter) are comparable to one another (>99.9 vs 99.49%, respectively), and slightly greater than that of the samples taken directly from the reservoir. Analysis of the carbon beds revealed that 0.51% of the smoke generated from the exposed DOP was composed of 2-ethyl hexanol.

Finally, the distribution of particle sizes in the aerosols generated from the ATI DOP penetrometer

are presented in tabular and graphic forms in Tables IV and V, and Figure 6. The data revealed that the geometric mean diameters of the particles generated from the fresh and exposed DOP samples were 0.224 and 0.244 microns, respectively. The particle size histograms are similar to one another, with forty-four percent of the aerosol particles generated from the fresh sample and fifty-three percent of the aerosol particles generated from the exposed sample ranging in size from 0.26 to 0.34 microns.

Discussion of Results

The aforementioned observations and analyses revealed that although DOP becomes brown in color after prolonged exposure to the conditions in the ATI DOP Penetrometer (336 hours at $167 \pm 2^\circ\text{C}$), very little decomposition occurs (< 1%). The fresh DOP has a calculated purity of 99.11%, while the exposed sample has a purity of 98.49%. These findings are not surprising. According to Farrer¹ and Nass², DOP is considered to be stable at temperatures greater than 200°C for extended periods of time. This is the primary reason that it is used as a plasticizer for polymers which are extruded and molded at temperatures exceeding 200°C . Farrer¹ and Nass² have stated that DOP should not decompose by more than 1% at $167 \pm 2^\circ\text{C}$. Unfortunately, neither could specify a time period.

DOP is a Newtonian fluid with a zero-shear rate viscosity approaching 8.14 Pascal-seconds. Although it was not quantified, the fresh and exposed DOP samples have comparable flow characteristics. This also suggests that little decomposition had occurred in the exposed sample.

Analysis of the data strongly suggests that the trace impurities within the fresh DOP react to a higher molecular weight hydrocarbon to produce a brown color (found within the exposed sample). More specifically, gas chromatography-mass spectrometry revealed that the lower molecular weight impurities within the fresh DOP are unreacted 2-ethyl hexanol and an ethyl hexyl benzoic acid ester, a "partially reacted phthalic anhydride." The trace impurities found within the exposed DOP are phthalic anhydride, and a high molecular weight hydrocarbon. The less intense carbonyl stretching found within the infrared spectrum of the exposed sample suggests some cleavage of the C-O bonds of the ethyl hexyl benzoic acid ester or DOP itself to

produce phthalic anhydride. Also, the less intense C-O stretching and more intense C-H and C-C stretching found in the infrared scan of the exposed sample are probably associated with the cleavage of the C-O bond of the 2-ethyl hexanol which is subsequently polymerized to a higher molecular weight hydrocarbon. This hydrocarbon is manifested by the "shoulder" (near 16 minutes) in the gas chromatogram for the exposed sample. According to Farrer¹, only a few tenths of one percent of a high molecular weight organic compound will produce a brown DOP solution which absorbs radiation in the visible region.

The smokes (aerosols) generated from the fresh and exposed DOP have purities which are slightly greater than that of samples removed directly from the reservoir. The impurities found in the samples taken directly from the reservoir are lower in molecular weight than DOP. The generation of smoke is analog to a distillation process. It is very possible that once volatilized, very little of these impurities condense (nucleate and grow) at $167 \pm 2^\circ\text{C}$.

Only small differences were noted in the distribution of sizes for the aerosol particles generated from the fresh and exposed DOP samples. The geometric mean diameter of the particles from the exposed sample was 8.9% greater than that from the fresh sample, and its geometric standard deviation was only 2% greater than that for the fresh sample. Under the non-adiabatic conditions found within the ATI DOP Penetrometer, classical nucleation theory^{3,4} indicates that the number and size of the aerosol or vapor particles (DOP in this case) depends primarily upon the rate of homogenous nucleation and growth of the particles. Nucleation and growth are inversely proportional to the temperature of the airstream and proportional to the activation energy barrier. See

Table IV. Distribution of particle sizes within DOP aerosol.

Particle size (micrometer)	Fresh DOP count value (# particles/cc of measured smoke)	Exposed DOP count value (# particles/cc of measured smoke)
0.123	8558	5908
0.129	8443	4541
0.135	9080	5064
0.141	12363	7905
0.147	12577	7230
0.155	17138	10636
0.165	17210	10660
0.175	19208	12052
0.185	23996	15565
0.195	27062	17952
0.205	28258	19760
0.215	26728	20341
0.225	23573	19770
0.235	19810	19131
0.260	122745	84149
0.300	71252	121102
0.340	16704	30621
0.380	6734	13878
0.420	2345	8211
0.460	848	4092
0.500	371	1456
0.540	237	406
0.580	184	103
0.680	534	52
0.840	92	5
1.000	11	0
1.160	2	1

Note: The listed values are the average of three measurements.

Table V. Geometric mean diameter and standard deviation of aerosols.

Sample	Geometric measurement run	Geometric mean diameter (micrometer)	Standard deviation
Fresh DOP	1	0.223	1.297
	2	0.224	1.299
	3	0.226	1.298
Exposed DOP	1	0.244	1.323
	2	0.244	1.326
	3	0.244	1.324

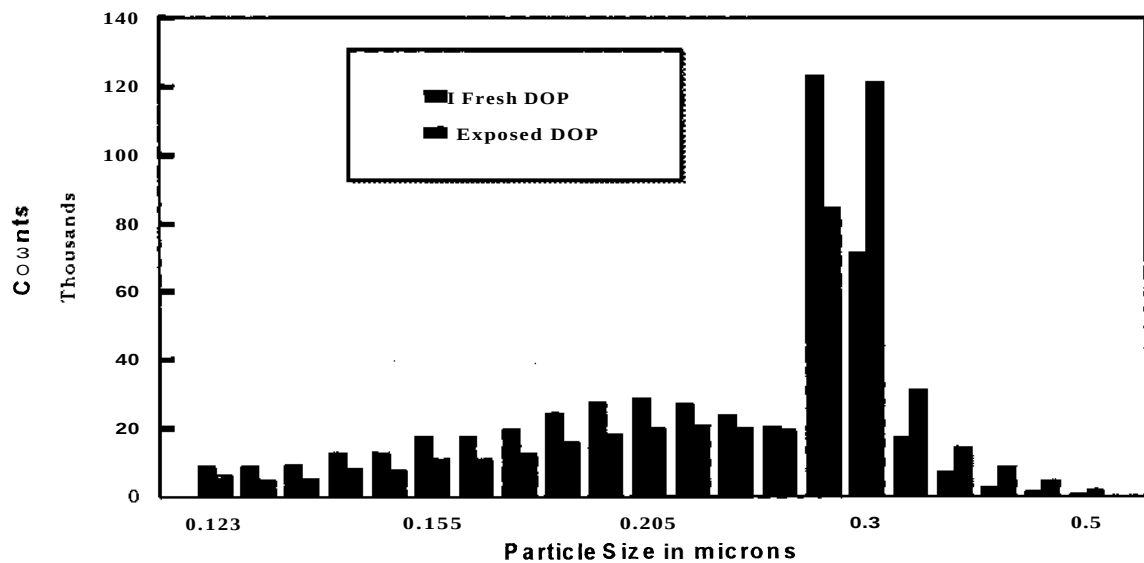


Figure 6. Distribution of particle sizes generated from fresh and exposed DOP.

Equations 2 and 3. Consequently, small differences which exist between the particle size distributions, geometric mean diameters and standard deviations for the fresh and exposed DOP samples are due to slight differences in the aerosol temperatures, rather than differences in the purity or chemical structure of the samples.

$$\text{Nucleation Rate} = A \exp(-E_{a1}/RT) \quad (2)$$

$$\text{Growth Rate} = B \exp(-E_{a2}/R\Delta T) \quad (3)$$

where A and B are empirically derived constants, E_{a1} and E_{a2} are the activation energies for nucleation and growth, respectively, R is the Universal gas constant, T is the absolute temperature of the airstream and ΔT is the degree of undercooling (difference between the airstream and DOP temperatures).

Conclusions

In conclusion, testing and analysis by several analytical techniques revealed that dioctyl phthalate (di[2-ethylhexyl] phthalate) experiences very little decomposition (99.11% for fresh vs 98.49% for exposed) after prolonged conditioning (336 hours at $167 \pm 2^\circ\text{C}$) in the ATI DOP "Smoke" Penetrometer. Analysis also indicated that the brown color is due to the presence of a trace quantity (a few tenths of a percent) of a high molecular weight hydrocarbon produced primarily by the reaction (probably

polymerization) of the 2-ethyl hexanol impurity within the fresh DOP.

Finally, gas chromatography and light scattering measurements revealed that insignificant differences exist between the (high) purity and character (distribution of particle sizes, geometric mean diameter, and standard deviation) of the aerosol particles generated from the fresh and exposed DOP samples.

References

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