

DIESEL EXHAUST COMPOSITION and ODOR Studies*

R. H. LINNELL, Senior Chemist, W. E. SCOTT, President,
Scott Research Laboratories, Inc., Parkside, Pennsylvania

With increased interest in emissions contributing to air pollution further studies on diesel exhaust are desirable. The well known diesel exhaust odor has not as yet been satisfactorily explained. This odor remains as a problem in the minds of the general public and more information in this area is the major goal of our research.¹

Previous Investigations

Most of the information available on the composition of diesel exhaust is contained in the following publications. An early study² by the Bureau of Mines gives some data on diesel exhaust composition and later work³ gives data on CO, CO₂, oxides of nitrogen, sulfur oxides, aldehydes, and CH₄, together with some correlations with odor and eye irritation. Davis⁴ has studied aldehyde removal from diesel exhaust. A comparison of exhaust gases from diesel, gasoline, and propane powered vehicles has been made by Elliott, et al.⁵ Total aldehydes, formaldehyde, and oxides of nitrogen were measured and correlated with odor in a General Motors research report.⁶ Recently a study has been made of the effect of diesel locomotives on the atmosphere of a railway tunnel⁷ in which NO_x, total oxides of nitrogen, CO, CO₂, SO₂, aldehydes, and O₃ were determined. Polynuclear aromatics were also determined in a railway tunnel and it was concluded that the levels found were no greater than those to be expected from the ventilating air alone.⁸ Fuel injection and smoke from a diesel were discussed in a French report.⁹ Traces of several polycyclic aromatics were found in diesel exhaust by English workers.¹⁰ Diesel smoke was studied as a function of fuel and additives, road speed, and engine size by Howe¹¹ and a continuous measurement instrument for smoke reported at the same meeting.¹² Another report on diesel smoke was given by Hobson.¹³ Little, if any, benzo(a)pyrene was found in diesel exhaust by Commins, et al.¹⁴ Infrared emission was used to study

diesel combustion by Lyn.¹⁵ A toxicity study¹⁶ reports acrolein and NO₂ to a lesser extent as the most important irritants in diesel exhaust under light load, and NO₂ the most important irritant under moderate load. Bailey, et al.,¹⁷ have analyzed exhaust for several compounds; formic acid, formaldehyde, ozone, oxides of nitrogen, carbon monoxide, acetaldehyde, acetone, polycyclics, etc.

A good review of earlier work was given at the First International Congress on Air Pollution, New York City, March 1-2, 1955.¹⁸

Experimental

Sources of Exhaust

A two-cycle, six-cylinder engine typical of equipment for motor coaches in city or interurban use was used in all this work. It is supercharged and has a rating of 220 hp. Engine data are as follows: 4.25 in. bore, 5.00 in. stroke, 425.6 cu in. total displacement, and 17:1 compression ratio. Total exhaust volume will be very closely equal to total air intake which is a function of rpm; 500 rpm, 160 cu ft per min; 800 rpm, 260 cu ft per min; 1100 rpm, 350 cu ft per min; 1200 rpm, 385 cu ft per min; 1600 rpm, 500 cu ft per min, and 2000 rpm, 610 cu ft per min. The engine is loaded with a General Electric 400-hp induction dynamometer. Speed and load can be varied independently.

A No. 2, 50-cetane fuel was used. This fuel is 70.9% saturates, 8.7% olefins, 20.4% aromatics (all by ASTM D-1319 fluorescent indicator method), and 0.110% sulfur.

Instrumentation

Infrared spectra were run on a Perkin-Elmer Model 21 instrument which was equipped with NaCl optics. For low concentration gas samples dual 40-meter long path cells (57-liter volume) were used. Solution spectra were run in NaCl cavity cells compensated by a wedge cell.

Colorimetry was done with a Bausch and Lomb Spectronic 20 instrument.

Gas chromatography was done with a Perkin-Elmer Model 151 Vapor Frac-

tometer equipped with hydrogen flame and thermal conductivity detectors, and on a temperature programmed F and M Model 609 flame ionization instrument.

Fluorescence and activation spectra were run on an Aminco-Kiers Spectrophosphorimeter with fluorescence attachment.

Sampling

Since diesel exhaust contains some higher molecular weight compounds, losses on surfaces of sampling containers can be serious. High water content tends to aggravate this problem. After considerable experimental work with both glass and stainless steel sampling lines (heated and unheated) and sampling flasks, we have adopted the following technique. Samples were taken from a 1/4 in. slotted (1/8 in. X 3 in. slot) stainless steel pipe welded into the 3 in. exhaust pipe about 6 in. from the exhaust manifold. A standard taper glass ball was attached directly to the 1/4 in. stainless pipe and all sampling flasks were equipped with the proper glass socket to fit, thus eliminating sampling lines.

For direct gas phase analysis of the exhaust by infrared spectroscopy, an appropriate glass flask (2.0-6.8 liters depending on the diesel operational mode) was evacuated and attached to the glass sample ball and the sample taken. The sample was then flushed into the 57-liter infrared cell with purified, dry, and CO₂ free air or N₂. Extensive tests of this method showed it was reproducible and that alternative nonflushing techniques yielded lower hydrocarbon values.

For gas chromatography, samples were taken in evacuated one-liter glass flasks equipped with Teflon stopcocks. These samples were flushed by pre-purified N₂ into a stainless steel sample loop of about 8 ml volume with an 8 in. section of 1/4 in. stainless packed with 30% polyglycol 600 on C-22 firebrick at the outlet end, the whole trap being cooled in liquid oxygen. For introduction into the chromatography column the trap was placed in boiling water.

Oxides of nitrogen were determined colorimetrically as well as by infrared.

* Presented at the 55th Annual Meeting of APCA, Sheraton-Chicago Hotel, May 20-24, 1962, Chicago, Illinois.

Table I—Diesel Exhaust rpm-Load Study

Ppm (by Volume) Dry Basis

Rpm	Load	H ₂ O	CO ₂	CH ₄	CO	NO	NO ₂	SO ₂	C ₂ H ₄	C ₂ H ₆
500	0	15,370	16,900	32.2	352	42.4	52.5	6.80	5.48	2.5
	1/4	26,400	34,400	47.3	151	127	159	13.7	5.15	2.6
	1/2	36,300	51,060	52.1	195	364	296	8.66	10.4	2.2
	3/4	43,700	56,700	73.3	175	436	408	13.95	15.7	3.7
	Full	62,400	74,700	116	4800	506	348	31.2	85.4	8.1
1200	0	15,400	17,000	34.0	191	88.4	32.6	32.2	8.50	3.4
	1/4	20,400	37,300	53.4	211	323	187	10.2	13.8	7.6
	1/2	35,000	41,500	65.6	173	493	485	12.1	15.6	5.2
	3/4	43,200	71,400	71.5	370	619	271	8.97	18.0	26.2
	Full	59,800	97,500	86.5	4650	815	330	35.2	63.7	13.1
1800	0	19,800	17,000	42.5	425	116	38.2	3.32	23.2	6.2
	1/4	24,800	37,600	77.0	256	265	108	17.1	17.1	12.0
	1/2	33,700	53,500	52.8	238	303	194	27.6	13.8	4.3
	3/4	50,000	79,200	65.5	466	580	239	10.7	31.7	11.5
	Full	59,800	99,500	82.0	2240	955	281	23.0	49.5	20.4
2000	0	16,500	25,500	65.0	340	145	56.0	10.2	15.7	8.5
	1/4	30,600	26,600	77.4	322	294	117	21.6	24.1	19.6
	1/2	30,700	52,200	59.1	196	495	262	20.8	24.4	16.5
	3/4	44,900	77,100	61.4	241	840	203	44.8	26.3	10.0
	Full	57,600	142,000	53.6	1450	965	286	—	71.5	—

* Calculated from 3.4 μ as hexane.* High H₂O prevents measurement.* High CO₂ prevents measurement.

One-liter evacuated collection flasks were used for the phenoldisulfonic acid method, following the procedure of Ellis.¹⁴ In some cases NO₂ was determined independently, especially on diluted samples, by using the Saltzman¹⁵ method. For the Saltzman method samples were either flushed through the reagent in a coarse fritted bubbler or the reagent was used in a glass syringe into which the gas sample was drawn.

Particulate Matter

Particulate was collected on Millipore type AA filters using an Aerosol Universal Filter Holder with a 10.0 liter/min orifice. Since the Millipore filter is slightly soluble in organic solvent, glass fiber filters were used when solvent extractions were performed. A Gelman Hurricane Air Sampler, Model 18002, with 8 in. x 10 in. Type A glass fiber filters was used when subsequent organic extraction work was planned. In some work, using a filter holder of our own design, we used No. 934H Ultra Filters (glass fiber mfg. by Hurlbut Paper Company). Isokinetic sampling

conditions were not always achieved due to difficulties in pulsating flow of exhaust gases and widely different velocities at different engine modes of operation. We have done no particle size distribution work but some microscopic examinations indicate that the particles are mainly submicron; if this is true non-isokinetic sampling will not introduce a serious error.

Odor Panel

The ideal experimental environment for odor research might be considered as a room, completely odor free, with constant temperature and humidity, into which odorants may be introduced with precise control of concentration. The Olfactorium developed at Cornell University is close to this ideal.²¹ Such a facility is extremely expensive and it is not clear that the results from such an olfactorium justify the expense. We have constructed a room enabling us to maintain a constant very low odor level with control of temperature and humidity. Our odor panel room has plaster board walls painted with white

later paint (which seems to be odorless after several days drying), an asbestos tile floor, and a total volume of 1700 cu ft. Panelists are seated at a bench partitioned into three units and constructed next to the wall of an adjoining room with three small entrance ports for introducing samples. Air at 400 cu ft per min is blown through a Cambridge No. 4312-85 filter, through a Barneby-Cheney Model 7-FN charcoal filterfold unit, and thence into the room. A static pressure of 0.03 in. water positive is maintained in the room by the blower system.

For the threshold odor work, all samples were made up by dilution using Matheson purified dry air. Raw diesel exhaust samples were first diluted by a factor of 10 to 15 by flushing the samples into a larger flask with prepurified nitrogen. Subsequent further dilution was done by partial pressure methods using air. All pyrex glass equipment is used. Twenty-milliliter glass syringes were used for the gaseous odor samples. Each panelist received three syringes in an aluminum tray, one syringe contained the odorant and the other two contained air only. After preliminary work to establish rough thresholds, dilutions were computed using increasing concentrations on a logarithmic scale. For each threshold determination a series of concentrations was given to the panelist, always starting with a concentration below the threshold. When a panelist correctly selected the syringe containing the odorant in two successive samples the threshold was considered to have been reached.

Because of the very low concentrations used, extreme precautions to avoid contamination need to be taken. The NO₂ dilutions were checked by the Saltzman¹⁵ method. Oxidation of NO to NO₂ was shown to be negligible over the time of the experiments. In other cases the master gas solutions were checked by infrared, but the dilutions in the syringes were not.

Results and Discussion

Load-RPM Studies

Table I shows the results of an infrared study of rpm-load relationships. Table II shows results for the diesel exhaust used in the odor panel work. The CH absorption has been reported as total hydrocarbon as hexane using the 3.4 micron infrared absorption. From a standpoint of ppm by volume, the values do not change much with rpm-load.

The oxides of nitrogen values reported in Tables I and II are of the same order of magnitude as those reported by other workers.^{2, 11, 12} At low rpm, low load conditions, temperatures in the diesel are low and formation of oxides of nitrogen is not favored. As

Table II—Diesel Exhaust Used for Odor Panel

All Values Ppm (by Volume) Dry Basis

	500 rpm ^a 0 Load	1800 rpm ^b Full Load
H ₂ O	15,300 ± 3050	73,100 ± 7080
CO ₂	9360 ± 3065	91,600 ± 10,300
CH ₄	58.1 ± 12.6	44.8 ± 5.5
CO	261 ± 41.4	2,510 ± 413
NO	93.3 ± 19.8	652 ± 116
NO ₂	43.8 ± 8.26	399 ± 30.0
SO ₂	6.81 ± 3.05	3.69 ± 4.20
C ₂ H ₄	15.5 ± 3.6	46.6 ± 7.0
C ₂ H ₆	6.5 ± 2.2	17.2 ± 4.6
Acrolein	4.01 ± 0.71	8.15 ± 0.96
Formaldehyde	4.57 ± 0.47	15.4 ± 4.0

^a Values given are average of 10 determinations on different days; average deviation given.

^b Values given are average of 3 determinations on different days; average deviation given.

* Calculated from 3.4 μ band as hexane.

Ppm (by Volume) Dry Basis

Rpm	Load	H ₂ O	CO ₂	CH ₄	CO	NO	NO ₂	SO ₂	C ₂ H ₄	C ₂ H ₂
500	0 (Cold)*	6,750	<4000	8.4	25.2	42	<1	<1	<1	<1
500	0 (Hot)*	15,800	<4000	60	382	59.5	3.4	5.5	<1	<1
1500	Full	14,500	4250	63	234	42.4	15.3	<1	<1	<1

* Flow measurements indicate about 0.4 ft³ blowby at 500 rpm and 2.4 ft³ blowby at 1500 rpm.

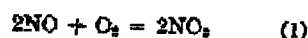
* Calculated as hexane.

* Sample taken on cold engine after starting.

* Sample taken on hot engine which has been run under load prior to the idle (500 rpm, 0 load) condition.

the rpm and load increase, temperature also increases, so that oxides of nitrogen strongly increase. At full throttle the excess oxygen, over that required for complete combustion of the fuel, is at a minimum. This limits the formation of oxides of nitrogen.

Our finding of substantial amounts of both nitric oxide and nitrogen dioxide might at first thought seem rather surprising. In automobile exhaust nitric oxide is the principal oxide of nitrogen present. Nitric oxide is the only oxide of nitrogen which possesses a sufficiently large equilibrium constant of formation at combustion temperatures to be formed in significant quantities.²² Excess air will oxidize nitric oxide to nitrogen dioxide, according to the reaction:



At parts per million levels of nitric oxide, in air, the rate of reaction (1) is very slow and the reaction has a negative temperature coefficient.²³ At room temperature, 200 ppm of nitric oxide in air will require about 30 minutes to be one-half converted to nitrogen dioxide. At higher temperatures or lower concentrations it will take longer. At the high compression ratio of diesel engines, concentrations will be very high. This concentration effect coupled with the excess air normally used in diesel operation will greatly accelerate reaction (1) and this probably explains the high nitrogen dioxide values found. Spark-ignition engines usually operate at lower compression ratios and without excess air so that high concentrations of nitrogen dioxide are not found.

Nitrous acid forms in diesel exhaust

due to the relatively high concentrations of nitric oxide, nitrogen dioxide, and water.



Absorption at 11.55 and 11.73 μ is substantially free of interference (small nitrogen dioxide interference) and characteristic for nitrous acid. The nitrous acid band system at 12.65 μ suffers from more nitrogen dioxide interference. Weak absorption at 2.95, 3.02, and 3.20 μ , which disappears when samples are passed through a dry ice trap, is almost certainly due to water. For the nitrous acid equilibrium in equation (2) the equilibrium constant, K , has been determined as 1.74 atmos⁻¹ by Wayne and Yost.²⁴ It can be computed from the values in Tables I and II that nitrous acid should be present in quantities up to several parts per million in raw diesel exhaust.

Both acetylene and ethylene increase with load but the very large increase in ethylene concentration at full load is striking.

Some concentrations found in blowby are given in Table III. The only significant component appears to be the CH₄. Since blowby volume is very small compared to exhaust volume, it would appear that there is no important contribution from blowby.

Acceleration samples are difficult to obtain on a reproducible basis without elaborate instrumentation. Table V gives typical results obtained without the use of automatic sampling devices. The significant finding here appears to be the substantially increased CH₄ and ethylene; there does not seem to be any large increase in either formaldehyde or

Table IV—Diesel Exhaust Acceleration Analysis*

Ppm (by Volume) Dry Basis

H ₂ O	CO ₂	CH ₄	CO
55,000-94,500	45,000-131,000	95-248	216-4750
NO	NO ₂	C ₂ H ₄	C ₂ H ₂
450-874	171-340	130-264	5.3-38
Acrolein		Formaldehyde	
2.9-9.3		7.0-32	

* Acceleration from 1100 rpm-83 hp to 2200 rpm-77 hp. Because of difficulty in obtaining a good sample, minimum and maximum values for 3 different samples, taken on different days, are given.

* Calculated from 3.4 μ as hexane.

Formaldehyde and acrolein have been prominently associated with both od and eye irritation in air pollution studies. We have determined acrolein by the 4-hexylresorcinol method²⁵ as formaldehyde by the chromotropic acid method.²⁶ In both methods we collected exhaust directly into the reagent in a fritted glass bubbler. Sample collection should be made as close as possible to the diesel and no cold sampling lines are permissible. For acrolein, two bubblers in series were used at first but when over 95% collection efficiency was found in the first bubbler the second bubbler was discontinued. There is some interference from the high nitrogen dioxide concentrations but at the 80 μ absorption maximum of the acrolein 4-hexylresorcinol product the NO₂-4-hexylresorcinol product absorbs very weakly.

In our original formaldehyde work diesel exhaust was collected in 20 ml of 95% ethyl alcohol in the MSA midge bubblers (coarse frits) at dry ice temperature. There was a serious interference from nitrogen dioxide and a correction was worked out using knowns and measurement at 500 and 580 μ . This method did not work well since it was found that the nitrogen dioxide interference was time dependent and that nitrogen dioxide not only formed a colored product with the chromotropic acid but appeared to also react with the formaldehyde-chromotropic acid. Sample collection at room temperature directly into the reagent (20 ml of 0.1% chromotropic acid in sulfuric acid) proved most satisfactory. Nitrogen dioxide is apparently not very soluble in the sulfuric acid reagent and the interference from nitrogen dioxide is negligible. Collection efficiency is very high and only one bubbler is required.

In Table V we have collected the formaldehyde and acrolein values found

Table V—Formaldehyde and Acrolein in Diesel Exhaust

Ppm (by Volume) Dry Basis

Rpm	Load	Formaldehyde	Acrolein
500	0	5.6	4.0
	1/4	4.0	3.9
	1/2	2.6	2.8
	3/4	2.4	4.2
	Full	23.4	11.4
1200	0	8.3	5.2
	1/4	4.3	2.2
	1/2	3.1	3.6
	3/4	3.7	3.0
	Full	12.8	9.7
1800	0	9.2	3.6
	1/4	1.8	2.4
	1/2	3.1	1.6
	3/4	2.3	2.4
	Full	20.2	10.6
2000	0	4.9	4.1
	1/4	2.2	2.8
	1/2	2.8	2.7
	3/4	3.3	4.6
	Full	13.7	7.8

Table VI—Odor Thresholds for Nitrogen Dioxide
Ppm (by Volume)

Subject	Trials	Threshold*	Standard Deviation
A	9	1.41	0.38
B	9	2.43	0.67
C	5	3.05	0.33
D	6	7.58	0.70
E	8	3.40	0.42
F	7	6.18	0.96

* Arithmetic mean of the individual thresholds.

in an rpm-load study. Higher values for both compounds at zero and full load conditions appear to be characteristic. Similar results have been reported by other workers.⁴ The same effect is noted for carbon monoxide (Table I). At moderate rpm-loads, more complete combustion results. At maximum rpm-load, we are approaching the stoichiometric fuel-air ratio and local regions deficient in air cause incomplete combustion and thus increased aldehyde and carbon monoxide.

Particulate Matter Studies

Particulate matter loading has been previously reported¹ for the diesel engine used in the present study. Values of 50-200 $\mu\text{g/liter}$ of exhaust (dry basis) were reported. Roughly 10% (by weight) of the particulate was ash (major components: Cu, Fe, Zn; minor components: Al, Ca, Cr, Pb, Mg, Mn, Ni, Ag, Sn, Ti, Mo).

Particulate matter was collected on glass fiber filters, extracted with ethanol in a Soxhlet, made to known volume and then analyzed for formaldehyde and acrolein. Known ethanol-formaldehyde and ethanol-acrolein solutions subjected to the same procedure did not lose formaldehyde or acrolein values. No acrolein was found in any of the samples. For three operating conditions of the diesel, formaldehyde was found as follows:

Rpm	Load	% by Wt.	Ppm (Vol./Vol.) of Exhaust
600	0	0.50	0.085
100	33 Hp	0.48	0.19
200	197 Hp	1.3	0.39

Purified N_2 was blown through the particulate on a glass fiber filter and hence into the formaldehyde reagent; no formaldehyde could be removed; ethanol extraction and colorimetric formaldehyde determination subsequently yielded the normal formaldehyde value. Particulate matter on glass fiber filters in evacuated flasks will leave brown NO_2 fumes on heating to 10°C but the fumes disappear on cooling.

These results indicate that no appreciable gas phase concentration changes for acrolein or formaldehyde will result

Table VII—Odor Thresholds of Diluted Diesel Exhaust and Computed Concentrations at Odor Thresholds

Subject	Trials	Air/Exhaust*	Ppm NO_2 **	Ppm CH_4 **	Ppm Acrolein*	Ppm Formaldehyde*
I. 500 Rpm, 0 Load						
A	4	215	0.20	0.27	0.010	0.021
B	4	385	0.11	0.15	0.010	0.012
C	3	205	0.21	0.28	0.020	0.022
D	4	140	0.31	0.42	0.020	0.033
E	6	190	0.23	0.31	0.021	0.024
F	5	300	0.12	0.16	0.011	0.013
II. 1800 Rpm, Full Load						
A	7	480	0.86	0.10	0.018	0.034
B	8	475	0.84	0.09	0.017	0.032
C	4	215	1.85	0.21	0.038	0.072
D	4	175	2.28	0.26	0.046	0.088
E	6	195	2.08	0.23	0.042	0.079
F	3	320	1.25	0.14	0.025	0.048

* Volume of dilution air per volume of raw diesel exhaust at the odor threshold.

** Computed by dividing concentration values in Table II by the threshold air/exhaust dilution ratio.

* Calculated from 3.4 μ band as hexane.

from particulate removal. The implications in terms of eye irritation and odor levels are not clear. These experiments were performed in preparation for eye irritation and odor work which has not yet been done.

Further analytical work was done on the particulate matter by benzene extraction (Soxhlet) of the glass fiber filters and evaporation of the benzene at room temperature under vacuum with a gentle stream of prepurified N_2 . An oily yellow residue with a heavy "diesel" odor remained. Infrared spectra of CCl_4 and CHCl_3 solutions of this residue were very similar to diesel fuel with strong bands in the 3.4μ region, 6.1 – 6.2μ , 6.8μ , 7.2μ , 11.4μ , and 13.1μ . A broad band in the 3.0μ region, a shoulder at 3.65μ , a strong 5.8μ band, a weak 6.4μ band, and a broad weak band at 7.8μ indicate different compounds than are present in diesel fuel. Treatment of the extracts with NaOH produces a dark color and some precipitation; infrared then showed removal of the bands at 3.0μ , 3.65μ , 5.8μ , 6.4μ , and 7.8μ . Treatment of the extracts with solid Na_2CO_3 reduced the bands at 3.0μ , 5.8μ , 6.4μ , and 7.8μ and aqueous Na_2CO_3 extraction removed these bands as well as the 3.65μ shoulder. When the CHCl_3 solutions of the extracts were treated with PCl_5 the 5.8μ band split into 5.62 and 5.80μ bands while $(\text{C}_2\text{H}_5)_2\text{NH}$ treatment gave a 6.22μ band; these results are strong evidence for the presence of carboxylic acid.²⁵ Since we are dealing with a complex mixture no final conclusions can be drawn but the infrared results indicate the extracts are mainly hydrocarbon, both aliphatic and aromatic, similar to diesel fuel, with some evidence for the presence of aldehydes and carboxylic acids. Due to the collection technique, higher molecular weight compounds are indicated.

Gas chromatography on the oily resi-

due, using a temperature programmed silicone gum rubber column (50 – 275°C) gave peaks identical with those from the diesel fuel used; the higher boiling peaks were increased relative to the low boilers in the particulate extract sample as compared to diesel fuel.

Column chromatography and fluorescence spectroscopy were also used to further separate and identify the benzene soluble extracts from diesel exhaust particulate. For this work the oily residue was dissolved in CHCl_3 . After investigating several types of alumina, Camag (obtained from A. H. Thomas Co.) acidic (pH 4.5) chromatographic grade Al_2O_3 was used. The water content is critical for proper separations and was adjusted to the values indicated. The column was 1.6 cm inside diameter, 28 cm long, equipped with a Teflon stopcock, and water cooled with tap water (12 – 15°C). In each column separation 18 g of the appropriate H_2O content Al_2O_3 was put in the column, 0.50 g ether washed SiO_2 was added to the top, and the sample was introduced on 1.00 g of the same Al_2O_3 (samples were used containing 50 – 150 mg solids, in CHCl_3 solvent which was added to the 1.00 g Al_2O_3 and gently warmed to remove the CHCl_3). Elution was made with pentane and pentane-ether solvents with 10 ml sample collections. With 3.4% H_2O content in the Al_2O_3 and collection of some 50 to 60 fractions using increasing polarity of solvent from pentane to 30% ether to 70% pentane, the fluorescence and activation spectra for the benzene solubles from diesel particulate extract are very much like the diesel fuel itself. No serious attempt has been made to identify the compounds present but naphthalene, acenaphthalene, terphenyls, and pyrene are probably present along with several other fluorescent molecules.

polycyclics can be separated and eluted. This technique is similar to that reported by Sawicki¹² and co-workers. The details of our methods and analytical data on the composition of the particulate will be published later when this phase of the work is completed.

Gas Chromatography

We have reported some low molecular weight hydrocarbons (propane, propylene, *n*-butene, iso-butylene, isopentane, 2-butane, *n*-pentane, 1,3-butadiene, and 1-pentene) previously.¹ These can be determined by gas chromatography with a DMS column. The total contribution of these low molecular weight hydrocarbons to the 3.4 μ C-H found in the infrared can be computed to be 10 to 25%. The balance of the C-H absorption in the infrared must be due to other compounds. Total olefins (excluding acetylene, ethylene, and propylene) amount to 1 to 2 ppm by volume in diesel exhaust. The odor thresholds for these low molecular weight hydrocarbons are quite large so that they do not make an important contribution to diesel exhaust odor.

The diesel exhaust samples condensed with liquid oxygen were temperature programmed from 50 to 125°C on a four-meter polyglycol E-600 (on C-22 firebrick) column. Diesel fuel was run through the same column under comparable conditions. Of 47 compounds found in the diesel exhaust, 34 were shown to come from the diesel fuel. Except for the light hydrocarbons, acrolein and one other unidentified peak (probably an oxygenate, originally thought to be propionaldehyde), all major peaks in the diesel exhaust are found in diesel fuel. The ratios of heights or areas in diesel fuel compared to diesel exhaust are not all the same; benzene is a striking example since there is much more benzene in the exhaust than in the fuel compared to a hydrocarbon such as nonane or octane. In general however, the relative peak heights or areas are the same in the exhaust and the fuel and the similarities are striking. A number of minor components have been identified but all are present in very low concentrations. In some cases exhaust condensates (mainly water) have been used to obtain larger quantities, and a number of simple alcohols and aldehydes have been found. When exhaust condensates are used it is not certain whether chemical reactions have taken place which would change the exhaust composition. Subtractive techniques (ascarite, which removes aldehydes and mercuric perchlorate, which removes olefins) on diesel exhaust have shown that neither aldehydes nor olefins are important components of the exhaust.

Threshold values for six female panelists are given for NO₂ in Table VI. Sex has been reported as not a factor of importance in odor panel selection.¹³ For other odorants we have less extensive results, but the same panelists have shown thresholds for acrolein from 0.4 to 6.62 ppm and for formaldehyde somewhat higher.

The same panel was used for diesel exhaust odor studies using two diesel operation modes to yield widely different oxide of nitrogen values. Exhaust composition data are given in Table II. In Table VII we have summarized the odor panel work on diesel exhaust. If we calculate the difference between the average threshold dilutions for diesel exhaust resulting from the two diesel operating modes and apply the *t*-test at the 95% confidence limit,¹⁴ we find that the null hypothesis cannot be rejected. In other words the differences in average threshold were too small to justify a claim that the two different exhaust compositions lead to different detection thresholds.

In Table VII we have also computed the concentrations of NO₂, CH, acrolein, and formaldehyde present in the diesel exhaust at the threshold dilution. These data show that, (a) under the 1600 rpm, full load condition, the average concentration of NO₂ present in the threshold dilution of diesel exhaust is 38% of the average threshold for pure NO₂, (b) under the 500 rpm, no load condition, the average concentration of NO₂ present in the threshold dilution of diesel exhaust is 4.9% of the average threshold for pure NO₂, (c) for both types of exhaust the average concentration of acrolein and formaldehyde present at the threshold dilution of the exhaust is only one-tenth to one-hundredth of the thresholds for the pure compounds, (d) the average concentration of CH at the threshold dilution of 500 rpm, no load, diesel exhaust is larger than for the 1600 rpm, full load exhaust. Some tentative conclusions can be made from these findings:

(1) At the threshold dilution of diesel exhaust acrolein and formaldehyde are present in such small concentrations relative to the threshold concentration for the pure compounds that it is unlikely that they are major factors in the detectability of diesel exhaust.

(2) Under load conditions, with high NO₂ values, the amount of NO₂ present in the threshold dilution of diesel exhaust is large enough, relative to the threshold for pure NO₂, that it is more likely to be a major factor in the detectability of diesel exhaust than are acrolein and formaldehyde. Some other factors must be operating, however.

(3) At idle conditions diesel fuel as measured by the 3.4 μ CH absorption is

present in such large concentration relative to NO₂, acrolein, and formaldehyde that it is a likely suspect as a major factor in the detectability of diesel exhaust produced under the conditions.

It may seem surprising that 500 rpm, no load diesel exhaust has an average threshold for our panel which cannot be distinguished from the threshold of the 1600 rpm, full load exhaust. For individual panelists this is not necessarily true. This suggests that thresholds for NO₂ for our panelists may not yield the same ranking order as for some other odorants such as the compounds making up the CH hydrocarbon band.

These findings are the first results of a series of psychophysical experiments. The verification of the importance of NO₂ and CH in the detectability of diesel exhaust requires extensive further odor studies on pure compounds and mixtures. This is the planned next phase in our work.

Acknowledgments

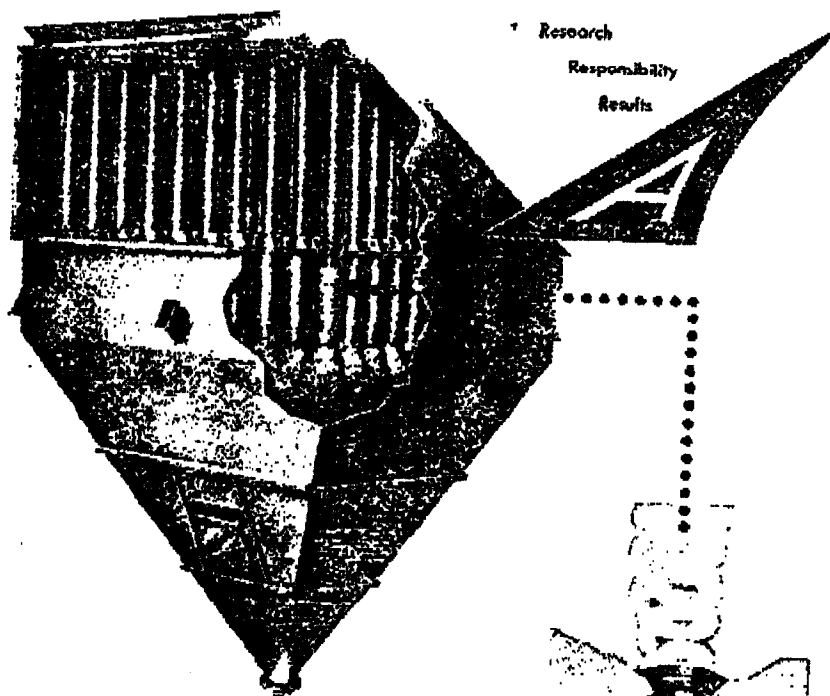
The work reported herein has been carried out under a research grant from the National Institutes of Health, Public Health Service, U. S. Department of Health, Education, and Welfare with assistance from the Coordinating Research Council, Inc. who have furnished engines, accessories, and technical and financial assistance in making this program possible.

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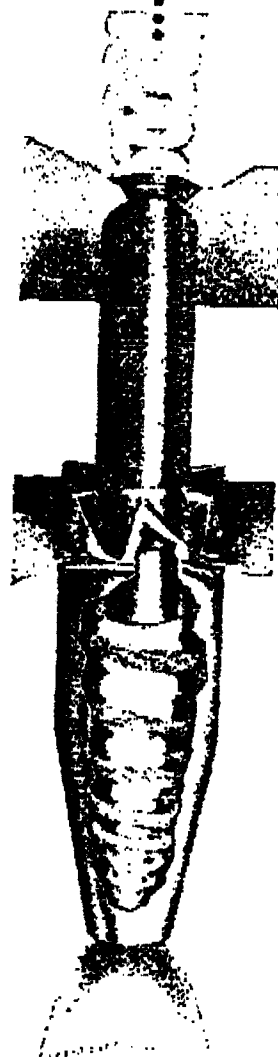
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SPOTLIGHTING THE SUSTAINER

Phillips Petroleum Company started in 1917 as a producer of crude oil and natural gasoline, with assets of only three million dollars and 27 employees. It became a refiner of crude oil and marketer of refined products in 1927.

Today, with assets of more than a billion and a half dollars and 25,000 employees, Phillips is exploring for crude oil and natural gas on six continents; it is a leading producer, refiner, and marketer of crude oil, natural gas, natural gas liquids, and their products; it utilizes all forms of transportation in a widespread network to gather its raw materials and distribute finished petroleum products throughout a large, growing marketing territory; its research organization is outstanding in the research-minded oil industry for the development of many new and improved products, processes, and methods; and it is one of the largest suppliers of petroleum chemicals.

The eighth largest U. S. oil company, Phillips is in first place in the petroleum industry as a producer of natural gas liquids, seller of natural gas, producer-marketer of liquefied petroleum gases, manufacturer of polyolefin plastics and of nitrogen fertilizers, supplier of raw materials to the rubber industry, and in atomic energy activities.

Phillips refined petroleum products are sold under the Phillips 66 shield at 22,000 marketing outlets in 40 states, the District of Columbia, and Canada.

Phillips Controls Air Pollution

Phillips chief problems and accomplishments in the field of air pollution control have been in its carbon black operations. As a leading supplier of carbon black, used primarily in tire manufacture, Phillips has the free world's largest oil furnace carbon black plant, located near Borger, Texas. In late 1960 the company completed a new carbon black plant near Orange, Texas. Phillips is part-owner of companies which have completed or are building carbon black plants in five foreign countries. The company's process for manufacturing carbon black is licensed by these companies as well as by companies in the U. S. and three other nations.

At the company's new Philblack Plant near Orange, Texas, a large amount of anti-pollution equipment was incorporated to completely eliminate air pollution. Included in this equipment are one 2385 glass filter bags, and an extensive vacuum cleaning system which, at the event of a carbon black leak in the operating area, sucks the black into the cleaning system until repairs can be made.

Each of the five overseas carbon black plants in which Phillips has an interest employs designs to reduce air pollution to a minimum.

Phillips began a smoke abatement program at its huge Philblack Plant near Orange in 1953. The first smoke abatement unit at this plant was placed in operation in February of that year. This unit was followed by a second unit in December 1953 and later units in February 1954 and July 1954. The final

unit was placed in operation in December 1960.

All of the units are equipped with bags made of fiber glass. Combustion gases from all units of the plant are virtually filtered and free from smoke when they are released into the air.

As a part of the smoke abatement program, all of the earlier filters have been enlarged and modernized and are in continuous operation. Other improvements have been made throughout the plant to eliminate leaks and spills.

This entire program eliminated the problem of air pollution from the Philblack Plant.

Upon completion of this program the editor of the local newspaper made this statement in his column:

"Fully appreciating the cost and the difficulties that had to be overcome in order for the Phillips Petroleum Company to convert their oil burning carbon black plants to white smoke, we join in the community-wide expression of gratitude as we happily observe this evidence of progress."

The newest filter is an example of the type of units Phillips has installed. It consists of a structure approximately 25 feet by 100 feet, and is comparable in height to a six-story building.

It contains 1120 bags, 26 feet long and 11½ in. in diam. The bags are made of a heavy glass cloth and all of the combustion gases from the unit pass through these before being released into the atmosphere.

The bags effectively filter out all carbon, releasing only clean gases.

LAUREN B. HITCHCOCK ASSOCIATES

Chemical Engineers

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Technical Advisory

John H. Schaeffer

Richard O'Mara, O'Mara Associates
1111 Wilshire Blvd., Los Angeles 17, Calif.

60 East 42nd St., New York 17, N. Y.
YUkon 6-4628

2 East Main St., Richmond 19, Va.
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AIRKEM TRANSFERS EASTERN OPERATIONS

Airkem, Inc., manufacturer of Airwick and Airkem sanitation and odor control products for business and industry, has transferred its principal eastern manufacturing operations to a new plant located on Commerce Road, Carlstadt, New Jersey, effective October 1, 1962. It has been announced by Frank W. Conkling, president.

Cost of the new facility, which supersedes Airkem's present plant in The Bronx, New York, is \$500,000. All personnel at the company's previous plant have been transferred to the new facility.

Completion of the Carlstadt plant marks the first phase in a planned national expansion of Airkem's manufacturing and warehousing operations, Mr. Conkling said. Initially, it doubles Airkem's production capacity and results in economies through consolidation of bottling operations and increased efficiency of new equipment installed in the building.

Situated on a two and a half acre plant, the Carlstadt plant has an initial floor area of 27,000 square feet. Provisions for future expansion to twice this area were incorporated into the building's basic design. Principal construction materials are white brick and block, and prefabricated golden colored metal paneling.

Functions performed by Airkem at the Carlstadt facility include the mixing of odor counteractants, disinfectants and other products, bottling and packing, warehousing and shipping.

The plant was designed by Engineers Incorporated, Newark, New Jersey, and built by Joseph L. Muscarelle, general contractors, Maywood, New Jersey.

EXHAUST COMPOSITION

(Continued from page 515)

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