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Benzene Content of Petroleum Solvents

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There has been a recent interest in labeling regulations for solvents and chemicals. Several states have passed or are considering all-inclusive laws. The Manufacturing Chemists Association has advocated warning labels on all chemicals which can be considered fire, health, or accident hazards.

In Massachusetts we have had a law for approximately 20 years requiring the labeling of products containing benzene. This law was extended within the last 10 years to include carbon tetrachloride. In spite of the limited coverage of this law, its enforcement is not complete. and, in fact, as we shall show, some of the problems of interpreting even this simple law are extremely difiicult.

In the past we have from time to time analyzed solvents for their benzene content. Frequently solvents which were obviously primarily petroleum naphtha have turned out on careful examination to contain 1% or 2% of benzene. Our analyses of these samples have upon occasion been questioned. In one instance we went so far as to recover dinitrobenzene from the solvent after nitration, recrystallize it, and carry out a mixed melting point determination with a known sample of dinitrobenzene.

In general, our department has not made a point of enforcing the labeling of products in which benzene was presumably present as an impurity in such a concentration that the degree of hazard produced was problematical.

During recent years, however, there have been several downward revisions in standards oi permissible concentrations oi benzene vapor. The valu used in the Commonwealth at present is 35 parts per million (ppm) parts of air compared with 100 ppm when our Division was first founded. The value which we use for naphtha vapors is 1000 ppm.

If we tolerate a concentratioii oi 1000 ppm of naphtha. a benzene content oi below 3.5% n-ill be necessary (since the molecular volumes of benzene and hexane. etc.. are similar) ; otherwise our permissible level for benzene vapor will be exceeded. There is some question as to the soundness oi this procedure, but none the less it is the one that we will have to follow until evidence is ai-ailable indicating a truer method oi evaluating the vapor hazard in such a case.

The problem of the benzene content oi petroleum solvents. particularly with regard to the labeling requirements. was recently brought to our attention by one oi ihe petroleum companies. We decided *to* reevaluate this situation, and for this purpose a total of eight sainples of low-boiling petroleum naphthas were obtained. These were subjected to analysis by physical and chemical methods, with special emphasis on the benzene content.

Physical methods available included determination of hoiiing point. specific gravity, and refractive index. The boiling point itself tells us very little about the composition of a solvent inisture, because there are many hydrocarbons with boiling ranges between 50 C and 100 C and in the vicinity oi the boiling point of benzene, approximately SO C.

Specific gravity in conjunction with the boiling point tells us considerably more. However, the reiractive index. which, in general, parallels the specific gravity, is more conveniently determined. particularly when small quantities of liquid are available.

As is well known, the lighter iractions of petroleum consist of a wide variety oi hydrocarbons. Those present in the highest pro-

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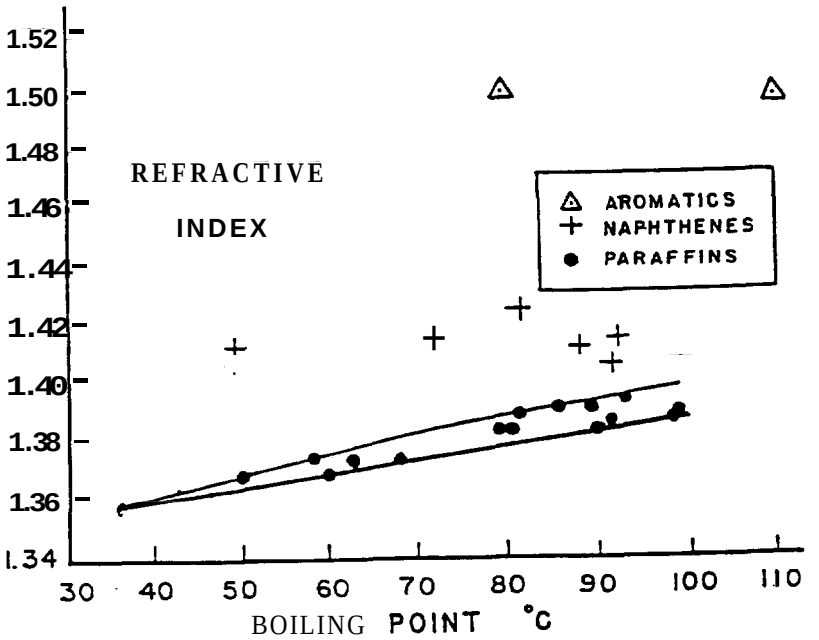

Fig. 1.—Refractive index and boiling point of individual hydrocarbons.

portion are in the paraffin group, so-called, having the formula C_nH_{2n+2}.

The naphthenes, or saturated cyclic hydrocarbons, are also present in petroleum in varying degrees. These include cyclopentane, cyclohexane, and several derivatives of cyclopentane which have boiling points below 100 C.

Finally, we have aromatics, of which benzene, boiling point 80 C, is the only one likely to be present in significant amounts in the highly volatile solvents.

In Figure 1 the refractive indices (R. I.) of several compounds in the paraffin series as well as naphthenes and aromatics are plotted against their corresponding boiling

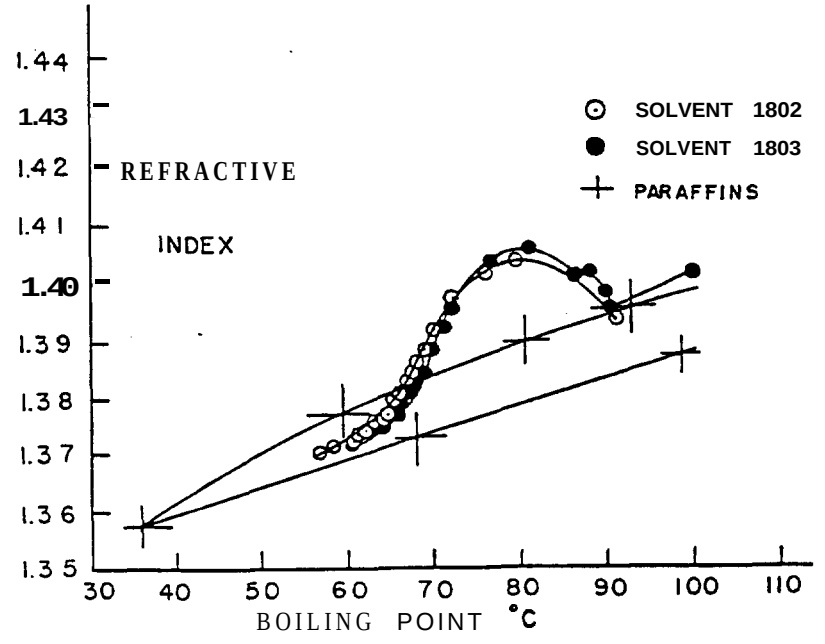

Fig. 2.—Refractive index-boiling point curve of petroleum naphtha solvents.

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It will be seen that the paraffins have the lowest R. I.'s, all below 1.395, and that the refractive index tends to increase with the increased boiling point.

With the naphthenes, refractive indices are considerably higher, being in excess of 1.4, and the increase in R. I. with increased boiling point is less pronounced than with the paraffins.

The aromatic benzene has a much higher refractive index than any of the other compounds listed, and it is slightly higher than that of toluene.

Our procedure in analyzing these solvents was to fractionate 200 ml. samples using a 30 in. fractionating column, determine the refractive index of each fraction, and plot the results against the boiling points. A solvent consisting purely of paraffinic hydrocarbons will be expected to show a steady rise in R. I. as the boiling point is increased. Any deviation would indicate the presence of naphthenes or aromatics, benzene in the case of solvents boiling below 100 C.

The naphtha samples we analyzed can be divided into three types, depending on their behavior on fractionation. The first has a rather wide boiling range, starting below 40 C and with the end-point around 110 C. The next group has a much narrower boiling range, the first fraction coming over around 60 C and with 90% distilled between 85 C and 90 C. Finally, there are the solvents designated as hexane, which are distilled for the most part between 60 C and 70 C.

When the refractive indices of the fractions were plotted against the mean boiling point, curves were obtained well above the area which paraffinic hydrocarbons would lie. In all cases in which the boiling point exceeded 85 C, a maximum refractive index was found, in most cases in the vicinity of 80 C. This corresponds, of course, to the boiling point of benzene, also, unfortunately, to the boiling point of cyclohexane. Figure shows R. I.-boiling-point curves for two solvents in Group 2.

We calculated the benzene content of the solvents, assuming that the bulk of the naphtha consisted of paraffins of the higher refractive indices and that the content of naphthenes was negligible. From these calculations benzene contents of from 1% to 10% were found for the different solvents.*

In addition, the solvents were tested by the chemical test used for determining benzene in air in which the hydrocarbon is nitrated and extracted with methylethylketone and color is developed by the addition of alkali.[7] In most cases several fractions were combined for these analyses.

Usually the results obtained by the chemical tests were lower than those obtained by refractive index calculations. We interpreted this to mean that the naphrhenic content of the solvents was considerable and thus threw off our assumptions as to the basic composition of the solvents. However, the chemical test did indicate concentrations ranging from 0.5% to 8% benzene in these same solvents, as shown in the Table.

As with the refractive index measurements, the benzene content determined chemically fell off sharply in the fractions with boiling ranges above 80 C. While toluene does interfere with the chemical test for benzene, inspection of the data of the Table shows that the aromatic contents of the highest boiling fractions tested, which would be expected to contain the most toluene, were as a rule insufficient to affect the final result materially.

We were fortunate in getting a check on two of these solvents in that the manufac-

*Sample calculation for fraction boiling at 81 C in Solvent 1803 (Fig. 2): R. I.'s benzene=1.500 fraction=1.406 corresponding paraffin=1.390. Benzene content of fraction=

$$\frac{1.406-1.390}{1.500-1.390}\times 100=\frac{0.016}{0.110}\times 100=14.5\%$$ by volume.

This calculation assumes the absence of paraffins of low R. I.'s and of naphthenes, as indicated above. Since this condition seldom exists, the results are not precise, but they usually give some indication of the approximate benzene content of the mixture. Other assumptions are that the various ingredients of the solvent form perfect mixtures (i. e., no volume changes occur) and that azeotropic mixtures are not produced. The first assumption is believed essentially correct; the second is probably incorrect and undoubtedly adds to the error of the determination.

Benzene Content of Naphtha Samples *

Sample No.	Fraction	Boning Range. C	Benzene Content of Fraction	Volume Per Cent of Entire Sample	Total
1801	All	36-112	Not done	...	...
	A	36- 68	2.1	0.8	...
	B	73- 81	3.8	0.4	...
	C	88- 94	1.5	0.2	...
	D	96-111	Not done	...	1.4
1806	All	36-114	2.5	...	2.5
	A	38- 65	1.6	0.5	...
	B	66- 69	4.2	1.0	...
	C	74	4.7	0.3	...
	D	92- 97	1.0	0.1	...
	E	100-111	Not done	...	1.9
				Mass spectrogram *	2.5
1802	All	50- 80	Not done	...	...
	A	57- 68	3.0	1.9	...
	B	6% 80	5.5	1.3	...
	C	91	Sot done	...	3.2
1798	All	50- 88	0.6	...	06
	A	?	?	0.05	...
	B	?	2.3	0.4	...
	C	?	0.6	0.03	...
	D	?	0.0	0.00	03
1799	All	61- 85	3.1	...	31
	A	61- 67	4.6	1.3	...
	B	67- 71	6.0	1.65	...
	C	72- 79	6.4	1.6	...
	D	85+ Residue	12	0.15	4.5
1803	All	61- 91	Not done	...	...
	A	61- 70	1.7	0.85	...
	B	71- 86	14	0.35	...
	C	88- 91	0.1	0.02	...
	D	95	Not done	...	1.2
1800	All	63- 70	1.8	...	18
	A	64- 66	19	0.7	...
	B	66-66	2.0	0.9	...
	C	66- 69	2.6	0.5	...
	D	Residue	4.5	0f	23
1807	All	63- 70	i.9	...	7.0
	A	63- 68	4.0	2.0	...
	B	68- 69	i.3	1.8	...
	C	69- 70	19.9	1.65	...
	D	77	6.6	0.35	5.8
				Mass spectrogram *	6.8

* Value supplied by manufacturer.

turer had made determinations with the mass spectrograph for the benzene content. The results were in good agreement with our chemical analyses.

In general, the benzene content of these solvents ranges from 1% to 4% in volume. It is not believed that the ordinary use of such solvents would produce benzene vapor hazards. Where the benzene content does exceed 1%, the supplier is in violation of the Massachusetts law if he fails to provide a warning label, however.

On the other hand, with solvents containing around 5% benzene, the possibility of substantial exposure to benzene vapors resulting in the free use of the solvent in question must be considered. Unless the other components of the solvent act to modify the effect of the benzene, use of such a solvent in processes such as fabric spreading, etc., might lead to excessive exposure to benzene.

In the air of one plant where hexane with a relatively low benzene content (1.5%) was used as a solvent in a fabric-spreading operation, a benzene vapor concentration of 1 ppm was found, compared with an average concentration of naphtha vapor, as determined by the combustible gas indicator, of 200 ppm.

SUMMARY

Methods of analysis of petroleum fractions for benzene are discussed. The results of such analyses of eight samples of naphtha solvents are given. Benzene concentrations range from 0.6% to nearly 7%. The hygienic significance of the benzene impurity in petroleum naphtha solvents is considered.

REFERENCE

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