1, 1-DIMETHYLCYCLOPENTANE AND 2-METHYLHEXANE IN A MIDCONTINENT PETROLEUM [1]

By Johannes H. Bruun [2] and Mildred M. Hicks-Bruun

ABSTRACT

This paper describes the separation and identification of 1,1-dimethylcyclopentane and of 2-methylhexane. The specific gravity, refractive index, boiling point, freezing point, and molecular weight of the isolated hydrocarbons are recorded and compared with the corresponding values for the synthetic hydrocarbons as reported in the literature. The infra-red absorption spectrum of the 2-methylhexane is shown. The 2-methylhexane is estimated to constitute about 0.25 per cent and the 1,1-dimethylcyclopentane not more than 0.04 per cent of the crude oil.

CONTENTS

	Page
I. Historical	465
1. C_7H_{14}, 1,1-Dimethylcyclopentane	465
2. C_7H_{16}, 2-Methylhexane	465
II. Experimental procedure and results	467
III. Discussion of the results	470
1. 1,1-Dimethylcyclopentane	470
2. 2-Methylhexane	471
IV. Acknowledgment	473
V. Bibliography	473

I. HISTORICAL

1. C_7H_{14}, 1, 1-DIMETHYLCYCLOPENTANE

1,1-Dimethylcyclopentane has apparently never been previously isolated from petroleum, nor does it seem that anybody claims to have established the presence of this hydrocarbon in any crude oil.

Synthetic 1,1-dimethylcyclopentane, however, has been prepared by Kishner (1),[3] who has reported values for its boiling point, refractive index, and density.

2. C_7H_{16}, 2-METHYLHEXANE

A study of the physical constants of known hydrocarbons reveals that a number of aliphatic and naphthenic hydrocarbons have boiling points which are near that (90.0° C.) reported for pure 2-methylhexane Because of this fact nobody seems to have succeeded in isolating the above hydrocarbon in a pure state from petroleum.

The presence of 2-methylhexane in petroleum, however, was indicated by the earliest investigators of petroleum, such as Pelouze and Cahours (2), Warren (3), and Schorlemmer (4). Since that time many investigators (5) have confirmed the presence of this isomer of *n*-heptane in petroleum and have also attempted to isolate the pure hydrocarbon. The physical constants of the final fraction, however,

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research associate representing the American Petroleum Institute at the Bureau of Standards.

[3] Figures in parenthesis here and elsewhere in the text indicate references given in the bibliography at the end of this paper.

indicate clearly that in every case considerable quantities of naphthene hydocarbons were present as contaminations.

Mabery (6) reported the isolation of a sample of "isoheptane" with a boiling range of 90° to 91° C. This sample was the result of 15 careful distillations, but the reported carbon-hydrogen ratio was too large to correspond to that of a pure aliphatic hydrocarbon.

Francis and Young (7) brominated the petroleum fraction which distilled between 93.5° and 102° C. and separated the normal and isoheptylic bromides by distillation under reduced pressure. They reduced the isoheptylic bromide with a zinc-copper couple and obtained a fraction which distilled between 89.9° and 90.4° C. This

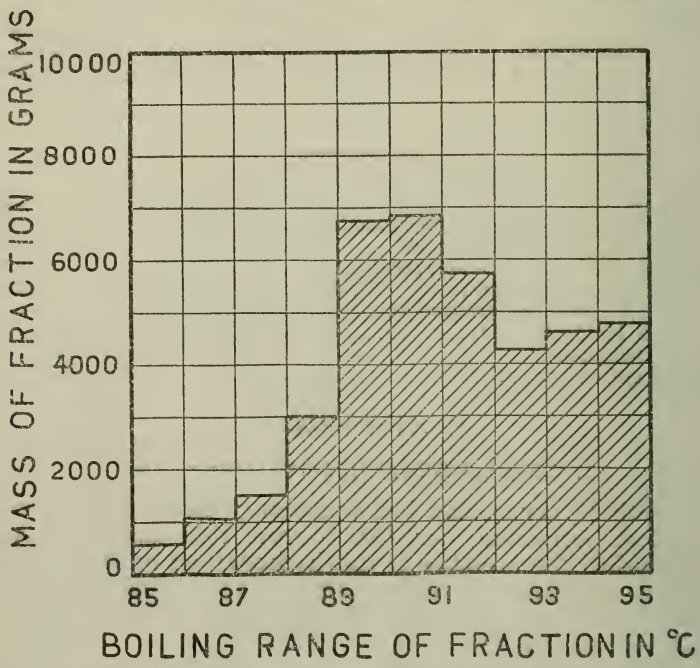

FIGURE 1.—*Distribution of the fractions over their boiling ranges before subjecting them to a nitrating treatment*

Ordinate: Mass of fraction in grams. Abscissa: Boiling range of fraction

had a specific gravity of 0.70670 $^{0°}_{4°}$ (corresponds to 0.6852 $^{25°}_{4°}$) as compared with 0.6746 $^{25°}_{4°}$ for pure 2-methylhexane.

Charitschkow (8) subjected a fraction of Grosny gasoline, with boiling range 90° to 93° C., to a nitrating treatment and subsequent heating with fuming sulphuric acid. He obtained a fraction which distilled between 90.5° to 91.5° C. and which had a specific gravity of 0. 7158 $^{15°}_{0°}$ (corresponds to 0.7079 $^{25°}_{4°}$). The vapor density agreed with the formula C_7H_{16}.

Later, Costaschescu (9) obtained from Roumanian petroleum by repeated distillation a fraction which he attempted to identify as 2-methylhexane. The boiling range and density of this sample, however, were respectively 91.5° to 92.5° C. and 0.7116 $^{0°}_{0°}$ (corresponds to 0.6951 $^{25°}_{4°}$).

Other investigators, who have later attempted to separate compounds from petroleum, have been content to merely comment on

the fact that while the isoheptanes are present in considerable quantity, their boiling points lie close together, and they show a marked tendency to form constant-boiling mixtures with other hydrocarbons and hence can not be isolated by physical methods.

II. EXPERIMENTAL PROCEDURE AND RESULTS

For the present investigation the Oklahoma crude petroleum used was that described in an earlier paper (10). The preliminary distillations [4] of the crude oil and of the fractions dealt with in this paper were carried out as reported in a previous publication (11). As a result of the preliminary distillations the petroleum fraction was distributed over its boiling range in the manner shown in Figure 1.

For the purpose of removing and determining the toluene which was present in the fractions, each cut was subjected to a nitrating treatment (12). The amount of material thus removed, however, was extremely small.

The subsequent final distillations of the fraction having boiling ranges between 85° and 95° C. were done almost entirely in the 11 m jack-chain column (13). About 2,000 ml of material was distilled each time, and the total distilling range for such a charge was often as low as a few tenths of a degree. For this reason special care had to be taken in mixing the distillates (according to their probable composition) for the redistillations. In most cases the boiling point, as well as the refractive index, was determined accurately for each fraction. After a great number of distillations in the 11 m column, a series of 0.1° and 1° C. cuts was obtained. In Figure 2 the distribution of these cuts is plotted against the boiling range. In this graph the amount in grams is given for each 1° C. cut. Thus, for instance, the sum of all of the 0.1° C. cuts with boiling ranges between 90° and 91° C. are shown as a single 1° cut. As shown in the graph, most of the material concentrated between 91° and 92° C., while, on the other hand, the fractions boiling between 85° and 90° and between 92° and 95° C. were comparatively small.

The refractive indices of the fractions, after the final distillations, are plotted against the boiling ranges in Figure 3. As shown by the graph, the highest refractive index (1.4101) was found for the material distilling between 87° and 88° C., while the fraction boiling between 90° and 91° exhibited a minimum (1.3947) in the refractive index graph.

In the case of the 87° to 88° C. cut, the amounts of available material were too small to permit isolation of the pure constituent. This fraction was subjected to a few more distillations in an efficient column, as a result of which the refractive index of the fraction distilling between 87.5° and 87.6° C. was raised to 1.4122. This fraction is discussed in Section III, below.

With regard to the 5,000 g of material with boiling ranges between 90° and 91° C., it was apparent (from the minimum exhibited by this fraction in the refractive index curve) that it consisted mainly of an aliphatic hydrocarbon. The molecular weight of this fraction was determined accurately (for method see (14)) and was found to be 99.6. From this value of the molecular weight, from the refractive index

[4] Acknowledgment is made to S. T. Schicktanz and assistants for all of the distillations referred to in this paper.

(1.3947) and from the boiling range of the material, it was concluded that 2-methylhexane was the major constituent. While pure 2-methylhexane is reported to freeze at −119.1° C. (15), our fraction did not freeze. By cooling, even at a very low rate, the viscosity of the material was tremendously increased, and instead of freezing to crystals a sirupy and glasslike substance was obtained, which could be pulled into long threads by means of a glass rod. In view of

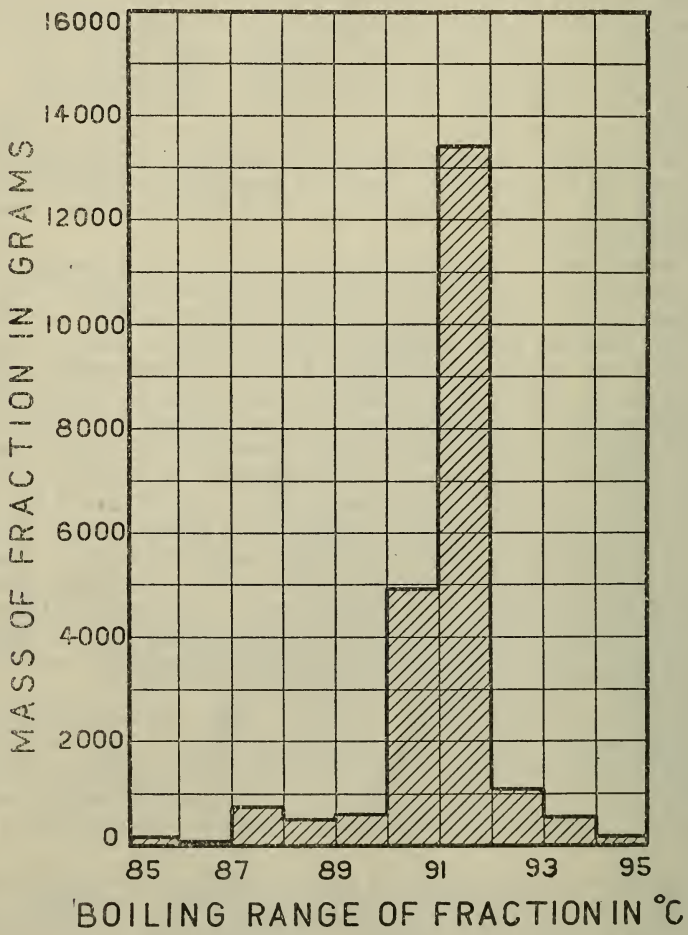

FIGURE 2.—*Distribution of the fractions over their boiling ranges after the final distillation*

Ordinate: Mass of fraction in grams. Abscissa: Boiling range of fraction.

the above fact it was apparent that further purification of the hydrocarbon could not be accomplished by means of simple equilibrium melting (16).

Attempts were made to separate the 2-methylhexane by preferential extraction. Aniline, sulphur dioxide, nitrobenzene, alcohols, and other solvents were tried, but without any appreciable amount of fractionation. Similarly, selective adsorption by means of silica gel, fuller's earth, charcoal, lampblack, and other materials was tried without success.

The method finally employed for the purification of the 2-methylhexane present in the 90° to 91° C. cut was that previously developed by R. T. Leslie (17) for the isolation of 2-methylheptane. The technic used was as follows: 100 ml of material to be fractionated was cooled by means of carbon dioxide slush and mixed with 120 ml of liquid propane. The liquid mixture thus obtained was further cooled by means of liquid air, after which it was slowly poured into

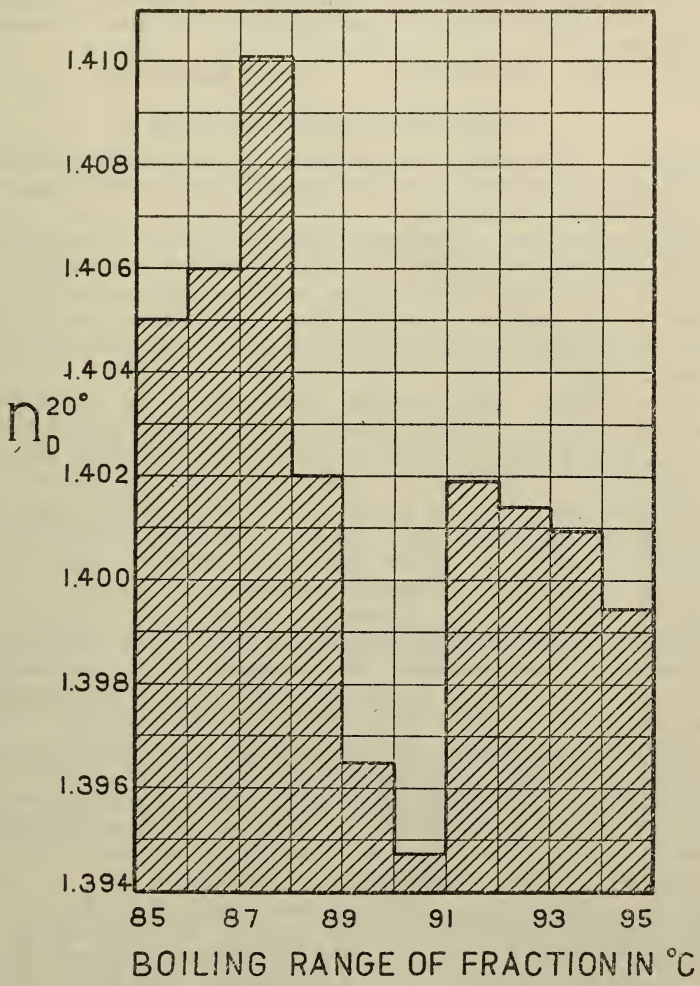

FIGURE 3.—*The refractive indices of the final distillates*

about 100 ml of liquid methane. Crystals would thereupon precipitate and these were separated from the mother liquor. After subsequent evaporation of the propane and methane, two fractions were obtained. The material which separated as crystals in the methane was found to be rich in 2-methylhexane. By systematic application of the above method, fractions of successively decreasing refractive indices were obtained.

As the fractionation proceeded, it was noticed that as soon as the refractive index decreased to below 1.393 the hydrocarbon would no longer form glass upon cooling, but would freeze easily to crystals. This, of course, indicated that the tendency to form a sirupy mass was not a property of the 2-methylhexane, but was caused by the impurities which were present in the 90° to 91° fraction.

The fractions which were obtained by the above method were mixed according to their refractive indices for further purification. In this way a sample of pure 2-methylhexane was finally isolated.

III. DISCUSSION OF THE RESULTS

1. 1, 1-DIMETHYLCYCLOPENTANE

Although 1, 1-dimethylcyclopentane was not isolated in a high state of purity, the evidence for its presence in the Oklahoma petroleum seems to be conclusive.

The first indication of the presence of the above hydrocarbon was shown by the graph in Figure 2. About 750 g of material distilled between 87° and 88° C., in other words, near the boiling point (87.5° C.) of 1, 1-dimethylcyclopentane, while less than 100 g of material was collected between 86° and 87° C., and less than 500 g between 88° and 89° C.

A second feature which renders the presence of 1, 1-dimethylcyclopentane highly probable is found in the fact that the 87° to 88° portion exhibits a very pronounced maximum (1.4101) in the refractive index graph. (See fig. 3.) By subjecting this cut to further distillation and by collecting a fraction having a boiling range of less than 0.1° C. at the boiling point (87.5° C.) of the pure hydrocarbon, the refractive index was further raised to 1.4122, or nearly to that reported for synthetic 1, 1-dimethylcyclopentane (1.4139).

While 1, 1-dimethylcyclopentane is the only known hydrocarbon for which the refractive index and boiling point agree with the petroleum fraction, there remained the possibility that our petroleum fraction was a mixture of an isomeric heptane, such as 2-methylhexane (boiling point = 90.2; $n_D^{20} = 1.385$), which has been isolated from the 90° to 91° cut (see p. 469) and of a compound with a higher refractive index, such as benzene (boiling point = 80.2; $n_D^{20} = 1.501$) or cyclohexane (boiling point = 80.8; $n_D^{20} = 1.476$), both of which have been found to be present in the petroleum used for this investigation.

However, the presence of benzene is excluded because of the nitrating treatment to which the material was subjected prior to the final distillation. Furthermore, additional treatments of the 87.5° to 87.6° cut with nitrating acid had no effect upon its refractive index.

If the 87.5° to 87.6° fraction ($n_D^{20} = 1.412$) were a mixture of cyclohexane and 2-methlyhexane, its composition, calculated from the refractive index, would correspond to 67 per cent of cyclohexane (molecular weight = 84) and 33 per cent of 2-methylhexane (molecular weight = 100). Such a mixture would have a molecular weight of 89.3.

The molecular weight was also calculated upon the previously mentioned assumption that the 87° to 88° cut consisted mainly of 1, 1-dimethylcyclopentane mixed with some 2-methylhexane. The composition of the 87.5° to 87.6° cut, calculated from its refractive index (1.4122) was thus found to be 95 per cent of 1, 1-dimethylcyclopentane (molecular weight = 98.1) and 5 per cent of 2-methyl-

hexane (molecular weight=100). The molecular weight of this mixture should be 98.3. If other isomeric heptanes with boiling points near 87.5° C., such as 3, 3-dimethylpentane (boiling point 86° C.; $n_D^{20}=1.391$) or 2, 3-dimethylpentane (boiling point 89.7° C; $n_D^{20}=1.392$), were present as minor constituents in the petroleum fraction (boiling point 87.5° to 87.6° C.; $n_D^{20}=1.412$) it is apparent that the percentage of 1,1-dimethylcyclopentane calculated from the refractive index would be less than 95, and consequently a somewhat higher value should be found for the molecular weight.

In view of the above facts it is apparent that any appreciable quantity of cyclohexane would reveal itself in a low value of the molecular weight. The experimental value, determined by measuring the freezing point depression in benzene, was found to be 102±4. This result agrees, within the experimental error, with the above calculated value for a mixture of 1, 1-dimethylcyclopentane and 2-methylhexane.

It seems that no value has been reported in the literature for the freezing point of 1, 1-dimethylcyclopentane. Because of this fact a freezing point was determined for our impure sample of the hydrocarbon. The sample was found to freeze to crystals at −76° C., but it failed to yield more than a slight break in its time-temperature cooling curve. Consequently, it was not of high purity. In Table 1 the physical constants of the fraction are given, together with the reported values for the synthetic hydrocarbon.

TABLE 1.—*Physical constants of 1,1-dimethylcyclopentane*

Sample	d_4^{20}	n_D^{20}	Normal boiling point	Initial freezing point (in dry air)	Molecular weight
			°C	°C	
Synthetic: Kishner (1)	0.7552	1.4139	87.5	----------	[1] 98.1
Petroleum fraction	[2] .7509	1.4122	87.5	−76.4	102±4

[1] Theoretical.
[2] Determined by the section for capacity and density of this bureau.

No definite value can be given for the amount of 1,1-dimethylcyclopentane present in the crude oil (600 gallons) but from the amount of the 87 to 88° cut (about 750 g) it is apparent that the percentage must be less than 0.04.

2. 2-METHYLHEXANE

The physical constants of the isolated sample of 2-methylhexane are given in Table 2, together with the best reported values in the literature. The high value found for the freezing point together with the flatness of the cooling curve (fig. 4) is an index of a high degree of purity.

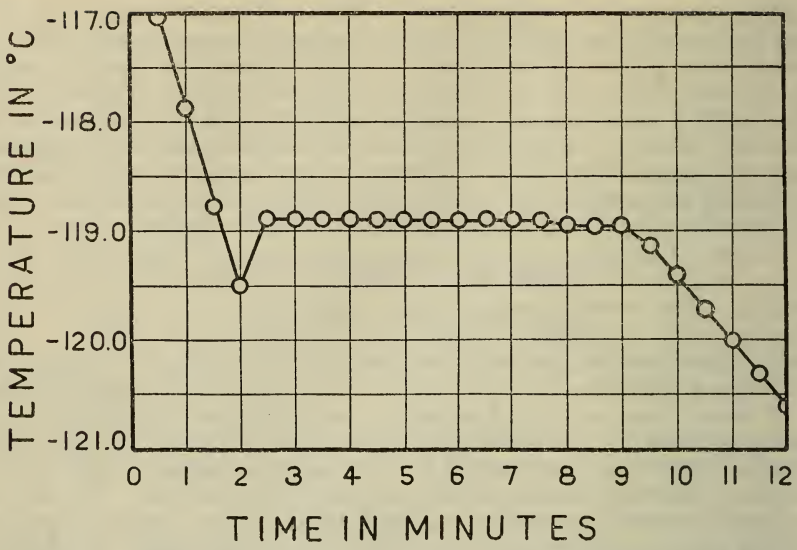

FIGURE 4.—*The time-temperature cooling curve of the 2-methylhexane isolated from petroleum*

TABLE 2.—*Physical constants of 2-methylhexane*

Sample	d_4^{25}	n_D^{20}	Normal boiling point	Freezing point (in dry air)	Critical solution temperature in aniline	Molecular weight
			°C	°C	°C	
Synthetic:						
Edgar and Calingaert	[1] 0.6746	1.38509	90.0	−119.1	74.1	[2] 100.0
Isolated from petroleum	[3] .67492	1.3850	89.67	[4] −118.90	74.1	[5] 100.0

[1] Computed from Edgar and Calingaert's value d_4^{20}=0.6789 and their value $\Delta d/\Delta t$ at 20° C.=0.000855.
[2] Theoretical.
[3] ±0.00001. Determined by the section for capacity and density of this bureau.
[4] Determined by means of a platinum-resistance thermometer.
[5] For method used see (14).

The freezing point, which is about 0.2° C. higher than that reported for the synthetic hydrocarbon, was determined by means of a platinum resistance thermometer calibrated by this bureau in accordance with the international temperature scale (18), as adopted in 1927.

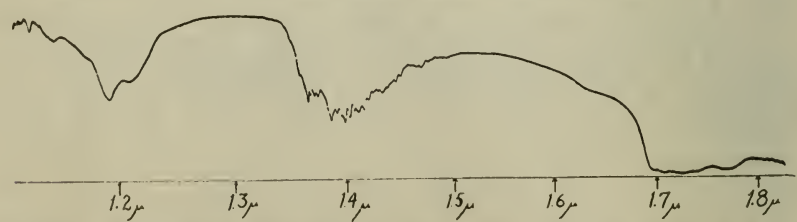

FIGURE 5.—*The energy transmission curve, through a 4 mm cell of 2-methylhexane, of the emission of a tungsten lamp source, recorded on an automatic registering infra-red spectograph*

Characteristic absorption of the hydrocarbon may be seen at 1.2, 1.4, and 1.7 μ. Fine structure bands at 1.1 and 1.4 μ are due to atmospheric water vapor. Recorded by U. Liddel, of the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture.

The infra-red absorption spectrum of our best sample was determined by U. Liddel, of the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture, and is shown in Figure 5.

From Figure 2 it is apparent that not less than 5 kg of 2-methylhexane was present in the petroleum fractions used for this work. Based upon the total amount of crude petroleum used (600 gallons, specific gravity = 0.9) it is estimated that the percentage of 2-methylhexane is not less than 0.25.

IV. ACKNOWLEDGMENT

The authors acknowledge the technical advice of E. W. Washburn, Director of American Petroleum Institute Project No. 6.

V. BIBLIOGRAPHY

1. Kishner, N. M., Chem. Zentr., vol. 2, p. 2132, 1913.
2. Pelouze and Cahours, Compt. rend., vol. 54, p. 1231; vol. 56, p. 505; vol. 57, p. 62.
3. Warren, C. M., Proc. Am. Acad. Art. Sci., vol. 27, p. 56, 1868.
4. Schorlemmer, C., Ann., vol. 136, p. 257, 1865.
5. References given in Engler-Höfer, Däs, Erdöl, vol. 1, p. 244, 1919, S. Hirzel, Leipzig.
6. Mabery, C. F., Proc. Am. Acad. Art. Sci., vol. 31, p. 55, 1894.
7. Francis, F. E., and Young, S., J. Chem. Soc., vol. 73, p. 921, 1898.
8. Charitschkow, K. W., Chem. Zentr., vol. 2, p. 474, 1899.
9. Costaschescu, N., Chem. Zentr., vol. 1, p. 682, 1911.
10. Washburn, E. W., Bruun, J. H., and Hicks, M. M., B. S. Jour. Research, vol. 2 (RP45), p. 469, 1929.
11. Bruun, J. H., and Hicks-Bruun, M. M., B. S. Jour. Research, vol. 7 (RP360), p. 608, 1931.
12. Bruun, J. H., Leslie, R. T., and Schicktanz, S. T., B. S. Jour. Research, vol. 6 (RP280), p. 364, 1931.
13. Bruun, J. H., and Schicktanz, S. T., B. S. Jour. Research, vol. 7 (RP379), p. 851, 1931.
14. Hicks-Bruun, M. M., B. S. Jour. Research, vol. 5 (RP215), p. 575, 1930.
15. Edgar, G., and Calingaert, G., J. Am. Chem. Soc., vol. 51, p. 1544, 1929.
16. Hicks-Bruun, M. M., and Bruun, J. H., B. S. Jour. Research, vol. 8 (RP432), p. 527, 1932.
17. Leslie, R. T., B. S. Jour. Research, vol. 9 (RP439), pp. 591–599, 1932.
18. Burgess, G. K., B. S. Jour. Research, vol. 1 (RP22), p. 635, 1928.

WASHINGTON, February 6, 1933.

161541—33——4