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THE DETERMINATION OF PRE-FORMED GUM IN GASOLINE

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The Determination of Pre-formed Gum in Gasoline

Historical

In the early days of the automotive industry gasoline was a mixture of very volatile hydrocarbons. It was distilled from crude petroleum, mostly of the "paraffin base" type, and was thoroughly refined by redistillation and by chemical treatment. As a result of its composition and treatment it was water white in color, sweet in odor, had an end point at about 300 F and when evaporated left no oily or sticky residue.

The demand for motor fuel forced manufacturers to use other materials for gasoline manufacture. They began to blend materials of higher end points with lower boiling components, and in 1913, upon the successful development of the Burton process for cracking gas oil, they began to place cracked gasoline on the market.

It began to be found that these gasolines had a tendency to deposit gummy and resinous substances in storage and in actual use in engines. Cracked gasoline, especially if carelessly made, was found to be a particular offender in this respect. However, the demand for motor fuel, and lately the recognized anti-knock value of the unsaturated hydrocarbons in cracked gasoline, has caused more and more cracked gasoline to be used, so that at at present a very large percentage of all gasoline is

manufactured by cracking heavy oils.

Introduction

The first mention of gasoline gum in literature was made by Hall[1] in 1915, who gave a description of it and further observed that it was apparently the result of oxidation. The first gum test or specification was reported by Dean[2] who states that it was devised by Robinson and his associates of the Atlantic Refining Company to be applied to aviation gasoline. For this test 100 cc of gasoline was evaporated to dryness in a hemispherical copper disk on a steam bath. This was a combination gum and corrosion test, in that it specified that the sample should not leave a weighable residue, neither should the disk be discolored due to the presence or free sulphur in the gasoline.

It was recognized at the time this specification was made that gasoline not passing this test would give satisfactory perfromance in a motor. The question now arose as to how much gum the gasoline could leave in the dish and still be satisfactory, so investigations began to be conducted for the purpose of answering this question.

It was soon found that the results obtained by this method were not reproducible, and efforts were made to improve the method. In 1922 Smith and Cooke[3] found that

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1. J. Inst. Petr. Tech. 1, 147, (1915)
2. Bur. Mines Tech. Paper 214
3. U. S. Bur. Mines Rept. 2394 (1922)

by evaporating the sample in a glass dish instead of a copper dish better checks were obtained. In 1925 Cooke[1] devised the steam over method in which samples were evaporated in silica or gaass dishes by steam in a steam atmosphere. This method gave reproducible results and proved very useful.

Later developments in the determination of gum in gasoline include a method[2, 3] in which samples are evaporated in an oven with a stream of gas (air, steam, or manufactured gas) blowing strongly over their surfaces; the method of Norris and Thole in which the sample is passed a drop at a time into a glass evaporating coil thru which a stream of nitrogen passes, giving the sample instantaneous evaporation; the method of Hoffert and Claxton[4] whereby oxygen at a definite rate is bubbled thru the sample under observation and the gum thus formed dried and weighed; the method of Voorhees and Eisinger[5] whereby the sample is put in a flask surrounded by steam and subjected to an initial oxygen pressure of 1.5 atm. gage - the fall of oxygen pressure in the flask giving the rate and extent of the oxidation of the sample and hence the tendency of the gasoline toward gum formation ;

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1. U. S. Bur. Mines Rept. 2686 (1925)
2. J. Inst, Petroleum Tech. 15, 643 (1929)
3. Littlejohn, Thomas and Thompson J. Inst. Petroleum Tech. 16, 684 (1930)
4. Report of the Joint Committee of the National Benzole Association and the University of Leeds (1929)
5. J. Soc. Automotive Eng. 24,584 (1929)

and a titration method developed by Yule and Wilson[1] which will be considered later.

Theory

Voorhees and Eisinger[2] distinguished between pre-formed gum (gum which is already in gasoline) and potential gum (a measure of the tendency of gasoline to gum in storage). Brooks[3] showed that cracked gasoline evidently reacts to form peroxides as an intermediate product, these peroxides reacting to give the resins which are commonly known as gums. Hardles and Moss[4], and Norris and Thole[5] have shown that even so-called pre-formed gum is not present in the form of gum, but mainly as intermediate products which are converted to gum under proper conditions.

The work of Voorhees and Eisinger[2] showed clearly that the pre-formed gums are the only ones that effect motor performances, these being generally deposited on and around the inlet valves. The potential gum is simply the amount of substance which will change to pre-formed gum under proper conditions; it may be looked upon as a measure of the stability of the gasoline during storage in regards to gum formation.

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1. Ind. and Eng. Chem. 23, 1254 (1931)
2. Ibid. 18,1198 (1926)
3. Loc. cit.
4. Loc. cit.
5. Loc. cit.

It would seem, then, that the determination of gum in gasoline should be divided into two distinct parts: the determination of the pre-formed and the determination of the potential gum.

The potential gum in a gasoline can be determined quite well. The oxidization of a number of samples by either the method of Hoffert and Claxton or that of Voorhees and Eisinger, which have been described, will give comparative results on the potential gum in the samples. A later method developed by Yule and Wilson[1] which consists in titrating the sample to obtain the amount of peroxide present gives good results.

The determination of pre-formed gum in gasoline is more difficult. Desirable conditions for such a determination which approximates the donditions under which gum is deposited in engines seem to be -

1. Instantaneous evaporation of the whole sample.

2. Evaporation at a temperature approximately equal to that of an inlet valve.

3. Maintenance of an accurately controlled temperature during the whole of the evaporation and exposure of every portion of the sample to the same temperature for the same period.

4. Exclusion of oxygen from the system because the effects of oxygen on gum formation are not well understood at the present.

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1. Loc. cit.

The determination of gum in gasoline by the evaporation of a sample in a dish does not fulfil these conditions. The evaporation is not instantaneous. The temperature at which the sample evaporates varies because the lighter fractions evaporate faster. Slight temperature differences in the dish during evaporation greatly affect the amount of gum deposited. Further, if the sample is exposed to oxygen during evaporation the oxidization of the gum varies; if the air above the sample is replaced by steam, the steam reacts chemically with the peroxides as shown by Yule and Wilson[1].

However, the test developed by Norris and Thole[2] closely approximates engine conditions. In this method a sample of gasoline (25 cc) is passed drop by drop into a spiral glass tube heated to about 200° C thru which is passed a current of nitrogen. The developers of this method found constant amounts of gum were deposited in the tube by the samples.

The Problem

A laboratory method of obtaining the absolute amount of pre-formed gum in gasoline was desired. It was hoped that a method could be found that could be used commercially in determining the characteristics of gasoline instead of the arbitrarily and generally unsatisfactory methods of gum determination now customarily used, i. e., the copper dish and the steam oven method.

Experimental

1. Loc. cit.
2. Loc. cit.

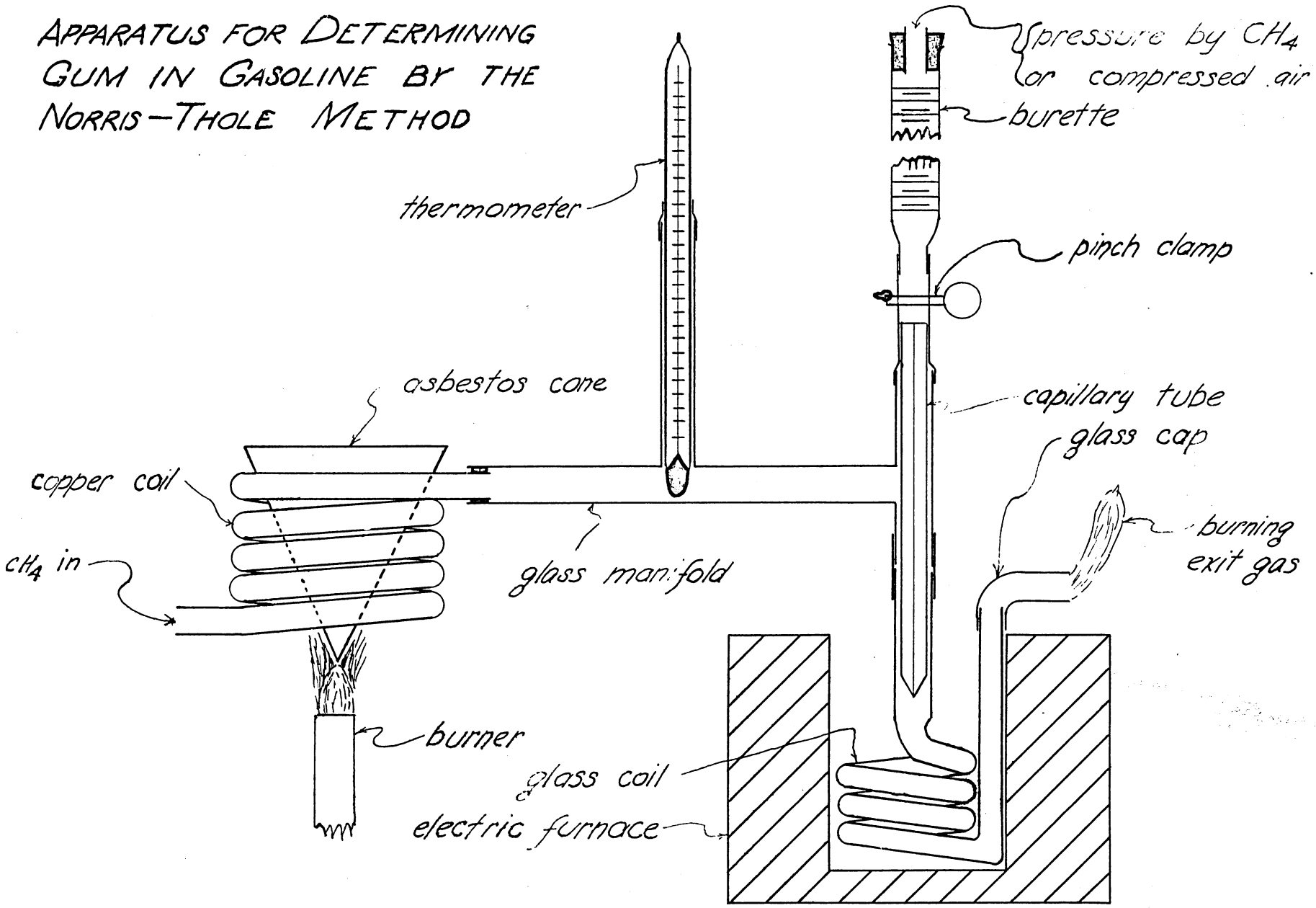
Experimental

It was believed that the method of instant evaporation developed by Norris and Thole, which approximates the conditions under which gum is formed on an inlet valve, could be used to give the absolute pre-formed gum in gasoline samples, and that such a method would be practical commercially.

Accordingly, a modified form of the apparatus used by Norris and Thole was constructed as is shown by the diagram. There was no nitrogen available to pass thru the apparatus, but there was available methane of 99% purity, so methane was used as the inert gas. For the interest of safety some method of getting rid of the combined methane and gasoline vapors emitted by the apparatus was necessary. It was decided that burning the exit gas offered the best solution to the problem. Accordingly a glass cap was fitted over the glass evaporation coil so the gases might be burned without leaving a deposit of soot on the exit of the evaporation coil.

The manifold by which the methane and gasoline were fed into the glass evaporation coil was constructed of 3/8" glass tubing, the evaporation coil itself was made of 1/4" glass tubing to which was welded a short piece of 3/8" tubing so it could be fastened to the manifold by a rubber connection. It was found convenient to use about a 40 cm. length of 1/4" tubing in making the coil, but to make sure the coil was long enough to cause all the gum to be deposited and none was being carried out the

Apparatus for Determining Gum in Gasoline by the Norris–Thole Method



apparatus by entrainment with the methane, a coil of 80 cm. length was made, so that it could be used as a check.

Preliminary tests were made with apparatus at temperatures of from 230° to 240° C. Samples of from 25 to 50 cc as other investigators had used were tried. However, it was found that such a small amount of gum was deposited from these samples that the errors in weighing the glass evaporator coil made it impossible to determine the amount of gum left by the sample. Accordingly a number of runs were made with 500 cc samples; it was found later that for some gasolines 250 cc samples gave enough gum to be determined quite accurately. The amount of gum obtained in evaporator coils made from 40 cm. lengths of glass tubing and in the one made from 80 cm. length was found to be the same. It was concluded from this that the apparatus was of the correct proportions to cause the deposit of all gum that should be deposited at that temperature.

While the gasoline was being evaporated the experimental conditions were recorded at short intervals. It was found that these conditions could be maintained approximately constant during the whole of a run. Table I. shown lists the data taken during the evaporation of a 250 cc sample to show how close to a constant value experimental conditions could be maintained during a run.

TABLE I

Temperature of inlet methane.	Temperature of evaporation coil	Gasoline evaporated	Time
C	C	cc.	min.
270	290	0	0
270	275	14	3
275	280	42	9
270	260	50	12
276	286	65	15
270	310	93	21
267	303	100	23
274	298	112	27
275	300	127	30
276	320	150	36
270	300	158	39
278	303	170	42
277	314	192	48
274	294	200	50
270	287	212	55
282	290	230	60
277	285	250	66

TABLE II

Sample number	Gum per 100 cc.		Factor
	copper dish method 100° C	Norris-Thole method 160° C	
1	0.0055	0.0003	18
2	0.0095	0.0004	26
4	0.0405	0.0015	27

Experiments were performed with four different samples. Two of the samples chosen were topped gasolines to which a small amount of cracked gasoline had been added for its anti-knock characteristics. The other two samples were liquid phase cracked gasolines.

Results

The gum these samples would deposit in the glass evaporation tube at temperatures ranging from 145° C to 390° C was determined. The results obtained were plotted; these results and curves connecting the plotted points are shown on the accompanying graph.

It is seen that the gum deposited by the topped gasolines varies only a small amount over a wide temperature range, while with the cracked gasolines a much greater amount of gum is deposited at the lower temperatures than at the higher temperatures. These results would seem to show that the gum deposited by some gasolines has an appreciable vapor pressure, a thing which Mardles and Moss[1] also demonstrated by evaporating gasoline samples in dishes at different temperatures and for different lengths of time.

It was desired to have a check on these results which show the amount of gum deposited is a function of the temperature at which it is deposited. Accordingly, a glass vacuum dessicator was equipped with a heating element so that a sample in a porcelain dish could

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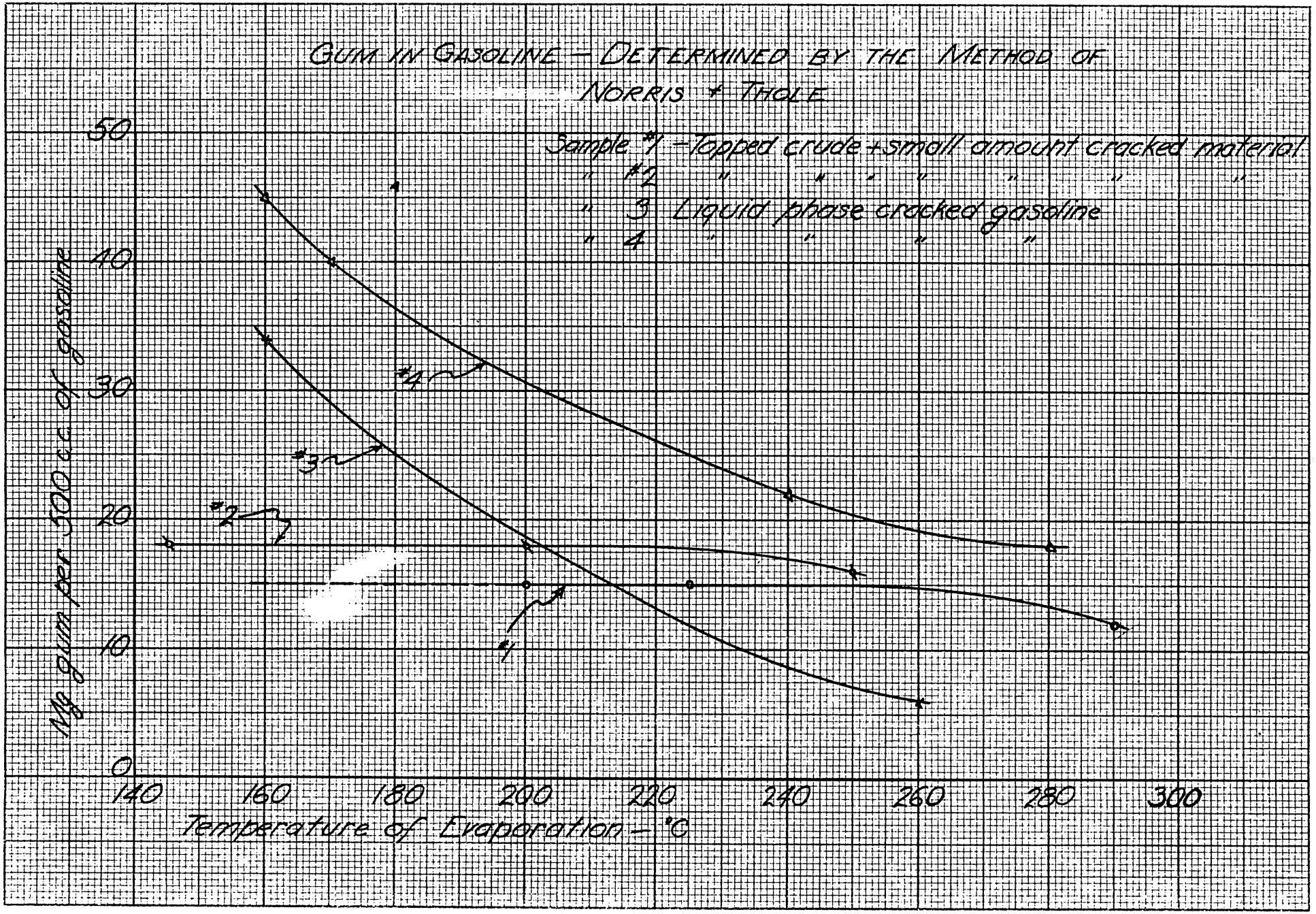
1. J. Inst. Pet. Tech. 15,657 (1929)


GUM IN GASOLINE – DETERMINED BY THE METHOD OF NORRIS + THOLE
Sample #1 – Topped crude + small amount cracked material
" #2 " " " " " " " "
" 3 Liquid phase cracked gasoline
" 4 " " " " "
Mg gum per 100 c.c. of gasoline
50
40
30
20
10
0
#4
#3
#2
#1
140
160
180
200
220
240
260
280
300
Temperature of Evaporation – °C

be evaporated without coming in contact with gases with which it would react. However, this equipment would not stand the high temperatures desired, so this check could not be made.

Samples of these gasolines were evaporated in a copper dish at a temperature of approximately 100° C. The results obtained as given by Table II show that approximately twenty-five times as much gum was obtained by this method as by the Norris-Thole method at 160° C.

Conclusions

From the results obtained by this experiment it would seem that to obtain the amount of gum that would actually be deposited in a motor, using the laboratory method developed by Norris and Thole; that the gum must be formed at a temperature closely approximating the temperature at which it would be formed in a motor. This shows that up to the present time no method of obtaining the absolute pre-formed gum in gasoline has been developed; when present methods are used the amount of gum deposited varies with the temperature.

However, in obtaining the characteristics of a gasoline a close approximation to the actual gum deposited in a motor seems to be obtained by the Norris-Thole apparatus, evaporating the sample at a temperature which is approximately the inlet valve temperature of the motor.