STUDIES IN POUR-POINT DEPRESSION OF WAX

by

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INTRODUCTION

The American Society for Testing Materials 1/ defines "pour-point" in its Designation 97-47. The definition states that the pour-point of a petroleum oil is the lowest temperature at which the oil will flow or pour when it is chilled without disturbance under definite prescribed conditions.

The conditions prescribed are to be rigidly followed. The oil to be tested is heated to a temperature of 115°F in a bath maintained at not higher than 115°F. The oil is then cooled to 90°F in an air or water bath at 77°F. Oils with a comparatively higher pour-point may be heated to a temperature 15° higher than the expected pour-point. The oil is heated in the specified jar in which the test is to be carried out. The jar is kept in the cooling-bath jacket, at the bottom of which a disc of felt or leather is placed.

After the oil has cooled enough to allow the formation of paraffin wax crystals, great care is to be taken not to disturb the mass of oil nor to permit the thermometer to shift in the oil. The cooling is further carried on and readings of the thermometer are noted at every multiple of 5°F. The test jar is carefully taken out of the bath and is tilted just enough to ascertain whether there is any movement of the oil. The complete operation of removal and re-

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1/ American Society for Testing Materials, Standard Method of Test for Cloud and Pour-Points: A.S.T.M.: D 97-47 Adopted 1928; Revised 1930, 1933, 1934, 1939, 1947.

placement is carried out in 3 seconds.

These tests are carried out in a series of baths that cool to progressively lower temperatures. When the oil has reached a temperature 50° higher than the succeeding bath, the sample is removed from the previous bath and transferred to the latter.

As the temperature of the oil sample gradually approaches the expected pour-point, the readings are taken at every 1° interval. As soon as the oil in the test jar does not flow on tilting the jar, the test jar is held in a horizontal position for exactly 5 seconds. If the oil shows any movement under these conditions, the jar is immediately replaced and the test is continued.

It is continued in this manner until a point is reached at which the oil in the test jar shows no movement when the test jar is held in a horizontal position for 5 seconds.

Limitations of Pour-Point Determinations

The effectiveness of the pour-point depressants is usually measured by the lowering of the pour test of the oil.2/ In the carrying out of such measurements, the limitations of the tests should well be understood. Both the pour and cloud test of an oil depend on the size, form, and rate of formation of the waxy crystals, which in turn depend on the previous history of the sample. In order to eliminate

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2/ Kalichevsky, A. V., Modern Methods of Refining Lubricating Oils: Am. Chem. Soc. Mono. Ser. 76, Reinhold Publishing Corporation, p. 171.

the latter variable, the sample is preheated to a relatively higher temperature before the test is started, in order to bring the wax crystals completely into oil solution.

According to Kalichevsky, 3/ Sachanen observed that the solidification temperature of oil varies with the temperature to which the oils were heated and that the higher preheating temperatures depress the solidification point, which rises, however, on storage to its original temperature. Chernozhuckov and Gutzait, 4/ recommend heating oils to 212°F. in order to eliminate the effect of previous treatments. Woof, Ganster, and Coulon 5/ find that if the oil is initially cooled at a very slow rate to -121°F and then reheated, the melting point is at its maximum, but rapid cooling does not give sufficient time for formation of wax crystals.

Heating the oil before testing may cause a change not only in its pour test but also in its specific gravity and viscosity. These three properties may be raised or lowered by preheating the samples, the change depending on whether the cooling takes place with the oil at rest or in motion. They are lowered or unaltered if the cooling is accompanied by stirring, and raised if the cooled sample is held at rest. Investigation of the crystal structure of separated wax particles substantiates the conclusion that these differences should be attributed to the differences in the size and the

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3/ Ibid., p. 171.

4/ Ibid., p. 171

5/ Ibid., p. 171.

quantity of the wax crystals present. While the above phenomena are not unusual with oils of Pennsylvania type, they are also observed with Mid-continent oils, which contain both wax and asphalt.

An interesting observation of Moerbeek and van Beest on the relationship of the sensitivity of pour-points to the thermal history of fuel oils showed that addition of small percentages of asphaltenes precipitated from residual fuels by pentane, to a residual fuel oil, the pour-point of which was insensitive to the temperature of pre-treatment, improved the sensitivity of this fuel to the pour test. On the other hand, removal of asphaltenes from fuel oils, which are in themselves temperature sensitive as to their pour-points, made such oils insensitive to temperature of pre-treatment.

The pour test of an oil with or without addition of a pour-point depressant may, in certain instances, show no differences when the samples are tested by standard procedure; whereas on slow chilling, samples containing the pour-point depressant may show a considerably lower pour point. Likewise all oil samples, particularly those containing pour-point depressants or very high melting-point waxes, may show a low cloud test when tested under standard conditions; whereas on slow chilling or on standing at relatively low temperatures for a certain length of time, they may develop a cloud due to separation of wax at higher temperatures than those which can be predicted from the cloud test.

Pour Instability or Pour-Point Reversion

It has been known for some time that motor oils were solidifying in their containers at temperatures higher than their A.S.T.M. pour-points.6/ This phenomenon was ascribed to critical winter temperature cycles. No failure of pour-depressant-treated oils has been reported in service in engines.

Because the extent to which paraffin-base oils are dewaxed by refines may be governed by various equipment and economic factors, the A.S.T.M. cloud points of various motor oils may range from 0°F to as high as 50°F. Field pour-stability data on these oils indicate a definite trend with decreasing cloud points. The most severe pour reversion is experienced with those motor oils having cloud points higher than 30°F. Those having cloud points from 18°F to 28°F average less pour reversion, and those having cloud points from 4°F to 18°F have no pour reversion. The pour-stability problem is therefore associated, to a limited degree, with oils of the intermediate cloud points, and, to a greater degree, with oils of the higher cloud-point range.

Different oils have different susceptibilities towards the action of a pour depressant. The amount of pour depressant used, therefore, will vary with different motor oils. Data gathered show that with different amounts of pour depressants, greater pour reversion occurs in oils with

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6/ Hodges, C. E., and Roy, A. W., Pour Instability: Oil and Gas Jour., pp. 89-91, Oct. 4, 1947.

higher cloud points. Although a lower A.S.T.M. point was obtained with a larger quantity of pour depressant, this quantity also had a detrimental effect on the pour stability in those cases. Pour instability of a treated oil depends also on the critical temperature cycles encountered during a winter storage period.

As the result of an extensive study carried out by the Standard Oil Development Company, a reliable laboratory procedure for measuring the pour-stability characteristics of winter-grade oils has been developed. It was found after 8 years of extensive acquisition of field data that the limited number of days on which sever pour reversion occurred was immediately preceded by 5 to 6 days of temperature sequences which all had the same general characteristics. It was found that there was a definite relationship between the level of temperature in these cycles producing pour reversion and the cloud points of these oils, the over-all temperatures being higher for high-cloud-point oils than for low-cloud-point oils. This S.O.D. test predicts the field performance of winter grade oils with a high degree of precision.

THE PROBLEM

The problem adopted for this investigation was to determine the effect of the addition of different liquids and solids on the pour-point of waxes. The importance of the problem can be judged from the fact that there are vast oil fields in certain parts of this country that yield crudes which have pour points of 70° to 90°F or more. These crudes predominantly contain waxes. In the temperatures that are encountered in those regions it can be imagined what difficulties the producers must be facing in transporting them to refineries, since the crude is likely to be in a solid state.

In view of the problem posed by these crudes and in an effort to gage the effect of addition of different substances on the behavior of waxes at low temperatures, this subject was taken up. The additives were chosen on the basis of molecular structures, molecular weights, low freezing points, and comparatively high boiling points. Some solids were also used to determine whether their effect would be comparable to that of adding low-fusing metals to high-melting metals to produce fusible alloys. Some solids were chosen on the basis of their known behavior in regard to depression of pour points.

When we take into consideration the utility of the findings of this investigation in the case of the above-mentioned crudes, it can be readily seen that substances which decompose on heating to produce compounds which are likely to cause considerable corrosion of the equipment--e.g., HCl and SO_2--should naturally be excluded. The compounds should also be not very volatile, because the object of their addition would be defeated by their evaporation. The economic feasibility of their use should also be taken into consideration.

Bearing in mind the above facts, the following classes of compounds were tried: aliphatic hydrocarbons, benzene derivatives, alcohols, naphthenes, ketones, petroleum fractions, vegetable oils, naphthalene derivatives, nitriles, and such other compounds as furfural, nitrobenzene, etc. The effects of these various compounds have been described in the part of this work concerned with the experiments.

THEORETICAL DISCUSSION

The definition of pour-point states that it is the temperature at which the liquid ceases to flow on solidification. It will be interesting to see why this flow ceases. As the liquid is gradually cooled down, it solidifies forming large crystalline bodies with an eventual formation of a solid mass. The rate of cooling, the state of relative motion or rest of the particles, and the presence of impurities are the causes which contribute to the formation of these crystalline bodies. Thus it can be seen that flow of fluid is intimately related to the formation of such large crystalline masses.

It is, therefore, imperative that if we have to depress the pour-point of a substance, we will have to influence the above-mentioned three causes which control this flow. The most important cause which lowers the pour-point is the presence of impurities. These impurities may act in any of the two ways i.e. either by preventing the formation of large crystals or lowering the melting point according to the relation given in van't Hoff's law of freezing point lowering.

A synthetic pour-point depressant acts quite effectively in very small quantities. The formation of large crystals is due to the fact that the molecules which form the crystals are held together by intramolecular forces. The synthetic pour-point depressant tends to introduce itself into the planes of these crystals and nullifies the effect of these intramolecular forces. This prevents the growth of large crystals. Thus it is evident that the liquid will flow at a lower temperature.

The second factor that influences the lowering of the pour-point can be explained on the basis of van't Hoff's law.

Consider a pure solid phase, such as ice, in equilibrium with a pure liquid phase, such as water, at some specified temperature and pressure. If the two phases are in equilibrium,

$$f_s = f_1^{\bullet}$$

where f_s represents the fugacity of the pure solid. If solute is added to the system, and if it dissolves only in the liquid phase and not in the solid phase, then the fugacity of the solvent will be lowered:

$$f_1 < f_1^{\bullet}$$

To re-establish equilibrium, f_s must be lowered also. This can be accomplished by decreasing the temperature. In that case, however, it is necessary to recognise that the fugacity of the liquid solvent will also be lowered by the drop in temperature, as well as by the addition of the solute. Nevertheless, equilibrium can be re-established if

$$df_s = df_1$$

or

$$d \ln f_s = d \ln f_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(a)}$$

Since the fugacity of the solid phase depends only upon the temperature, whereas that of the solvent depends both on the temperature and the concentration of the added solute, the total differentials of equation (a) may be expressed in terms of the appropriate partial derivatives as follows

$$\left[\frac{\partial \ln f_s}{T}\right]_P dT = \left[\frac{\partial \ln f_1}{T}\right]_{P, N_2} dT + \left[\frac{\partial \ln f_1}{N_2}\right]_{P,T} dN_2$$

The two temperature derivatives may be replaced by appropriate terms with partial enthalpies, and the remaining term by its equivalent,

$$\left[\frac{\partial \ln f_1}{N_2}\right]_{P,T} = -1.$$

Thus we obtain

$$\frac{\bar{H}^* - H_s^\bullet}{RT^2} dT = \frac{\bar{H} - \bar{H}_1}{RT^2} dT - dN_2 \;.............\; (b)$$

which may be rearranged to

$$dT = - \frac{RT^2}{H - H_s} dN_2 \;.......................\; (c)$$

$\bar{H}_1$ is the partial molal heat content of the liquid solvent; $H_s^\bullet$, the molal heat content of the pure solid form of the solvent. In such a case

$H_1 - H_s^\bullet$ is approximately equal to $H_1^\bullet - H_s^\bullet$ = heat of fusion of one mole of solvent

$$= \Delta H_{\text{fusion of solvent}}$$

Hence equation c may be re-written as

$$dT = - \frac{RT^2}{\Delta H_{\text{fusion of solvent}}} dN_2$$

The solvent used in this investigation does not seem to conform to this law as the calculated lowering and the observed lowering of pour-point for different concentrations of the solutes do not tally. This can be explained from the fact that the above-mentioned law is based on the fact that the solvent and solutes used in the experiments cannot be considered as perfectly pure. The wax sample under investigation is definitely not a pure substance but a mixture of similarly constituted hydrocarbons. A relation can be found on the basis of the above equation which will explain the observed values.

SEARCH OF LITERATURE

Natural Pour-Point Depressants

The possibility of discovering substances that are capable of lowering the pour-point of oils has been indicated by the effect of some of the oil constituents on the fluidity of wax-bearing stocks at low temperatures.[7] These constituents, which are of the asphaltic type, are removed from the oil in the course of deasphalting or solvent-refining operations because their presence in the finished products is objectionable because of their instability.

These constituents can be isolated, however, by a variety of methods--for instance, by percolating unrefined petroleum residue through clay and by displacing the adsorbed material with various solvents. Fractions obtained from such filters, on being washed with naphtha, appear very similar to the last portions of the oil passed through the filters. Fractions obtained by subsequent washing of the filters with benzene are, in contrast, resinous in nature, but their pour-point depressant qualities are practically absent. However, materials removed from the filters by further washing with alcohols or similar solvents exhibit distinct pour-point depressant tendencies. Substances of similar nature can also be isolated by employing liquid precipitants such as low-molecular hydrocarbons or aliphatic

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[7] Kalichevsky, A. V., Op. cit., p. 169.

alcohols. Unfortunately, however, the quantity of such substances required for effecting the lowering of the pour-point is rather large (seven percent); and when added in the required amount, they have an unfavorable effect on other oil properties, such as carbon residue, oxidation stability, and color. Similar difficulties are also encountered in employing pour-point depressants obtained directly from such materials as cracking-still residue or distillation residue, hydrogenated tars from cracking processes, tar pitch, oxidized waxy hydrocarbons, and wax tailings.

Such inadequacies of natural pour-point depressants resulted in numerous attempts at synthesizing various compounds that when added to the oil would possess good pour-point depressant qualities without impairing other desirable oil properties.

Synthetic Pour-Point Depressants

In a compilation of this sort it is impossible not to mention a number of references of doubtful pertinence. For example, many of the patents do not unqualifiedly state that the pour-point is lowered. Others merely refer to satisfactory winter lubrication, which may mean that a pour-inhibiting action may be present or merely that a low-cold-test oil has been used without interference with its normal properties on the part of the additive substances.8/

8/ Byers, J. H., National Petroleum News, vol. 28, no. 49, Dec. 2, 1936.

The older patents are particularly obscure. They are more interesting from the standpoint of recognition of the difficulty than of assistance in solving the problem, although several seem to foreshadow modern developments. For instance, the patent granted to Eames and Seely shows that as early as 1867 the idea of adding a pour inhibitor to an oil was fully understood. The patent to Draper in 1880 represents a step in the same direction. Of course, many of the patents relate merely to dilution, the oil simply being thinned out at both ends of the scale.

The majority of the newer patents are of the synthetic type obtained by condensation or polymerization of hydrocarbons or related substances. Paraflow, patented by Davis (patent 1,815,022) in 1931 is a synthetic oil formed by condensation of waxy hydrocarbons with aromatic hydrocarbons. Paraflow inhibits the formation of wax crystals without affecting the viscosity-temperature characteristics. Smith (patent 1,944,851) suppresses the formation of a wax gel in paraffin-type oils by means of an agent obtained by heating petroleum oils in the presence of aluminum chloride. Maverick (patent 1,963,239) employs a condensation product of paraffinic hydrocarbons and aromatic hydrocarbons to improve the fluidity of gear oils at low temperatures. Schumen, Muench, and Ufer (patent 2,070,703) add polymerization products of vinyl ethers of unsaturated alcohols to lubricating oils, asserting that not only the setting point, but also the lubricating properties and viscosity index are favorably affected. Wulff and Brewers (patent 2,020,714) lower the setting point by adding polymerised vinyl esters of fatty acids.

Ralston, Christensen, and Selby (patent 2,033,546) describe an improvement that consists in adding a Friedel-Crafts reaction product from a higher fatty acid chloride and a coal tar fraction. Moran (patent 2,043,836) states that particularly effective pour-point depressants for oils containing waxy materials may be produced by the reaction, in the presence of anhydrous aluminium chloride, between oleic acid and any unsubstituted aromatic hydrocarbons.

There are also substances of direct mineral origin that will reduce pour points of lubricating oils. Pattin, (patent 318,389) as early as 1885 refers to a low-cold-test oil made by incorporating into the crude petroleum a sulfuric-acid-treated residuum. Davis (patent 1,917,875) adds wax tailings. Bonnel (patent 1,953,039) uses cracking coil tar. Levin (patent 2,024,106) obtains a pour-point depressant by extracting a cracking still residue. Cutis (patent 2,037,563) uses a material taken up by adsorbent earth from residual cylinder stock. Manly and Gross (patent 2,040,057) use a pour depressant consisting of an extract of pitch.

Soaps form an important group. Among these patented soaps may be mentioned the following: patent 1,594,762 (Van Gundy and Dimmig), patent 1,652,969 (Willcock, Caplan and Babb), patent 1,729,823 (Dimmig), patent 1,752,309 (Rossenbaum), patent 1,767,076 (Jarmann), patent 1,789,026

(Sullivan), patent 1,806,734 (Bennett, Story and Beckley), patent 1,806,735 (Bennett and Story), patent 1,820,295 (Bennett), and patent 1,837,279 (McGill). As a rule, soaps of alumina, lead, magnesium, and zinc are favored. The use of soaps to lower the pour-point is less actively followed than the use of the synthetic group. According to Dimmig, the basic lead oleate is not permanently soluble in hydrocarbon oils and does not reduce the viscosity at low temperatures. Bennet and Story point out that in adding soap to lower the pour-point a further problem is involved in maintaining or stabilizing the low pour-point.

Fatty oils have been used in some instances. Mackle (patent 1,677,244) describes an oil which may be employed at high or low temperatures in place of oils of different viscosities. Ott (patent 1,929,189) discloses a railroad-car journal oil that is efficient at operating temperatures varying 100°F to -50°F or lower. His claims are based on a mineral oil that is substantially insoluble in liquid sulfur dioxide and that is mixed with a small quantity of oxidized rape-seed oil. Cottonseed and lard oils are also mentioned. Bijur (patent 1,944,164) produces a low-pour-point-test oil from a vacuum-distilled bright-stock petroleum oil of low-carbon content and pour-point-test made from asphaltic crudes and free from paraffins, together with blown rape-seed, cottonseed, peanut, or corn oil.

Fatty acids, in some cases, lower the pour-points. Sullivan (patent 1,789,026) adds to the oils, acids obtained by oxidation of paraffin wax. McGill (patent 1,837,279) reduces the pour point by means of hydroxystearic acid. A product formed by esterifying dihydroxystearic acid by stearic acid also serves the purpose of a pour depressant.

Certain esters of diverse types are also used. For example, Hagedorn (patent 1,882,816) dissolves 9 parts cellulose naphthenate in 100 parts transformer oil which at 100°C has a viscosity of 1.0° Engler. Thereupon the oil exhibits a viscosity of 2.5° Engler, which remains constant at temperatures between -10°C and 30°C. Ellis (patent 2,018,758) discloses pour inhibitors that are esters formed by reacting alkylamines with organic acids. These not only act with lubricating oils but may also be used in greases. Wulff and Brewers (2,020,714) use the polymerized fatty-acid vinyl esters. Van Pesky employs compounds of the ester type obtained by condensing disaccharoses with aliphatic acids to lower the pour-point of waxy lubricating oils. Pevere (patent 2,039,111) prepares a lubricating oil having a reduced pour test from lubricating oil stock derived from mixed-base and paraffinic-base crudes by the addition of ethylene glycol distearate.

Several substances of the ether group have been used. Hickmann (patent 1,963,901) mentions cellulose ethers; Muench and Ufer (patent 1,984,421), polyglycol ethers; Schumann, Muench and Ufer (patent 2,020,703) and Wulff and Brewers (patent 2,020,714), polymerised vinyl ethers.

Chlorine compounds have an effect. Draper (patent

228,181) uses chloroform in minor proportions to lower the temperature at which the oil congeals. Oldacre (patent 1,604,068) observes that a cutting compound that has a low-cold test is preferable to the converse, and produced such a fluid by heating a mineral oil with sulfur chloride. Barnard (patent 1,796,857) employs carbon tetrachloride in the role of a solvent or a thinner. Henricksen and Lincoln (patent 1,959,054) report a low cold test in connection with the use of a very small amount of a chlorinated amide. McLaren (patents 1,963,917 and 1,963,918) asserts that stably bound chlorine atoms in a condensation-type pour-point inhibitor enhance the effect. Prutton (patent 1,986,651) states that the cold test of lubricating oil is lowered by the use of chlorinated carbon-ring compounds. Clark (patent 2,019,338) employs mixtures of chlorinated compounds of low pour-points primarily for transformers but also for lubricating oils.

The amines are represented by Sullivan and McGill (patent 1,870,074), Henricksen and Lincoln (patent 1,959,054), and Ellis (2,018,758).

Recently ketones have been found useful. Ralston and Christensen have made mention of these in patent 2,033,543.

The use of a pour-point depressant and the general characteristics of such products is discussed in connection with the description of Paraflow, one of the commercial products that is being marketed on a large scale. The discussion is also applicable to other pour-point depressants.

PARAFLOW

This is a commercial condensation product of chlorinated wax and naphthalene in the presence of aluminum chloride. It is marketed in oil solutions to permit careful adjustment of the pour-point depressant qualities by varying the amount of oil used as a diluent. When added to the oil in small quantities, such as 0.5% or less, it effectively lowers the pour-point without unfavorable effect on other oil properties. If, however, Paraflow is used in large quantities, such as 2% or more, it may increase the carbon residue of the oil and the rate of carbon formation in the engine. Its effectiveness can sometimes be improved if the oil has been previously refined from asphaltic and resinous impurities. This improvement in effectiveness, however, is of secondary importance, as Paraflow is always added to the oils after they have been subjected to the various treating processes. It should be noted, also, that oils containing Paraflow should not be further refined, because Paraflow may be removed from these oils during refining--for instance, by percolation through clay.

Paraflow is added to oils that have been already dewaxed to a relatively low pour test, such as 20°-25°F, in order to lower the pour test still further, to 0° or less. The use of Paraflow under these conditions permits the refiner to eliminate the use of low refrigerating temperatures and to avoid two dewaxing operations that are sometimes needed if conventional dewaxing methods are employed for attaining such low pour tests.

In general, the effectiveness of Paraflow decreases with the increase in the viscosity of the oil. Exceptions to this rule are known, however, and occasionally a residual oil is found that responds to the addition of Paraflow or a distillate stock of low viscosity is found that is inert to such additions. Apparently, however, Paraflow is most effective with paraffin and not with the ceresin type of waxes. The lower the melting point of waxes, the more efficient is the action of Paraflow.

It is of interest that Paraflow itself has a relatively high pour point. For this reason, addition of Paraflow to a wax-free distillate may actually result in an increase in the pour-point of such an oil. Addition of Paraflow to a wax-bearing stock may likewise first lower the pour-point and then raise it after the quantity of Paraflow added has reached the optimum point. This fluctuation is observed, however, only when very high quantities have been added to the oil, a type of addition which never occurs in commercial practice. The above behavior of Paraflow is illustrated by the following examples obtained with Coastal and Mid-continental distillate stocks of 58 and 140 Saybolt sec. at 100^{o}F respectively.

TABLE A

EFFECT OF ADDITION OF PARAFLOW ON THE POUR POINT OF OILS

Amount of Paraflow (% vol. in blend)	Pour Point	
	Coastal (F)	Mid-continent (F)
0	-70°	+10°
3	-65°	-25°
5	-60°	-50°
10	-55°	-40°
20	-50°	-30°
50	-25°	- 5°
80	- 5°	+ 5°
90	+10°	+10°
100	+20°	+20°

The above tabulation shows, therefore, that while Paraflow is capable of lowering the pour-point of the wax-bearing oils, such oils are themselves capable of lowering the pour-point of Paraflow.

It is generally agreed that the action of Paraflow is due to its ability to inhibit the excessive growth of wax crystals and to change the shape of the crystals from the needle type to small equiaxial grains of uniform size. Such small crystals do not interfere to any great extent with the flow of the oil, but they are still able to develop a higher cloud point. For this reason, although the pour-point is reduced by Paraflow, the cloud point of the oil is affected to a considerable degree, particularly when the oil contains high-melting-point waxes. In certain cases the differential between the pour and cloud points of an oil treated with Paraflow may become as high as $50^{\circ}F$ to $60^{\circ}F$, particularly with the coastal type of stocks of high-melting-point waxes.

In the search of the literature it was found that very little work has been done on the substances used in this work. Hence there is little information on the behavior of these substances in regard to pour-point depressant qualities.

EQUIPMENT

The following equipment (Fig. 1) was utilized in the tests:

a. Test Jar - A test jar 'a' of clear glass, cylindrical form, flat bottom, approximately 1 3/16 to 1 5/16-in. inside diameter and 4 1/2 to 5 in. in height

b. Thermometer - A thermometer graduated up to 300°F with 1-degree divisions

c. Cork - A cork 'c' to fit the test jar, bored centrally to take the test thermometer

d. Jacket - A jacket 'd' of metal, water-tight, of cylindrical form, flat bottom, about 4 1/2 in. in depth, with inside diameter 3/8 to 1/2 in. greater than the diameter of the test jar

e. Disc - A disc of cork or felt 'e' 1/4 in. in thickness and of the same diameter as the inside of the jacket

f. Gasket - A leather gasket, ring type, 'f' about 3/16 in. in thickness to fit snugly around the outside of the jar and loosely inside the jacket

g. A cooling bath

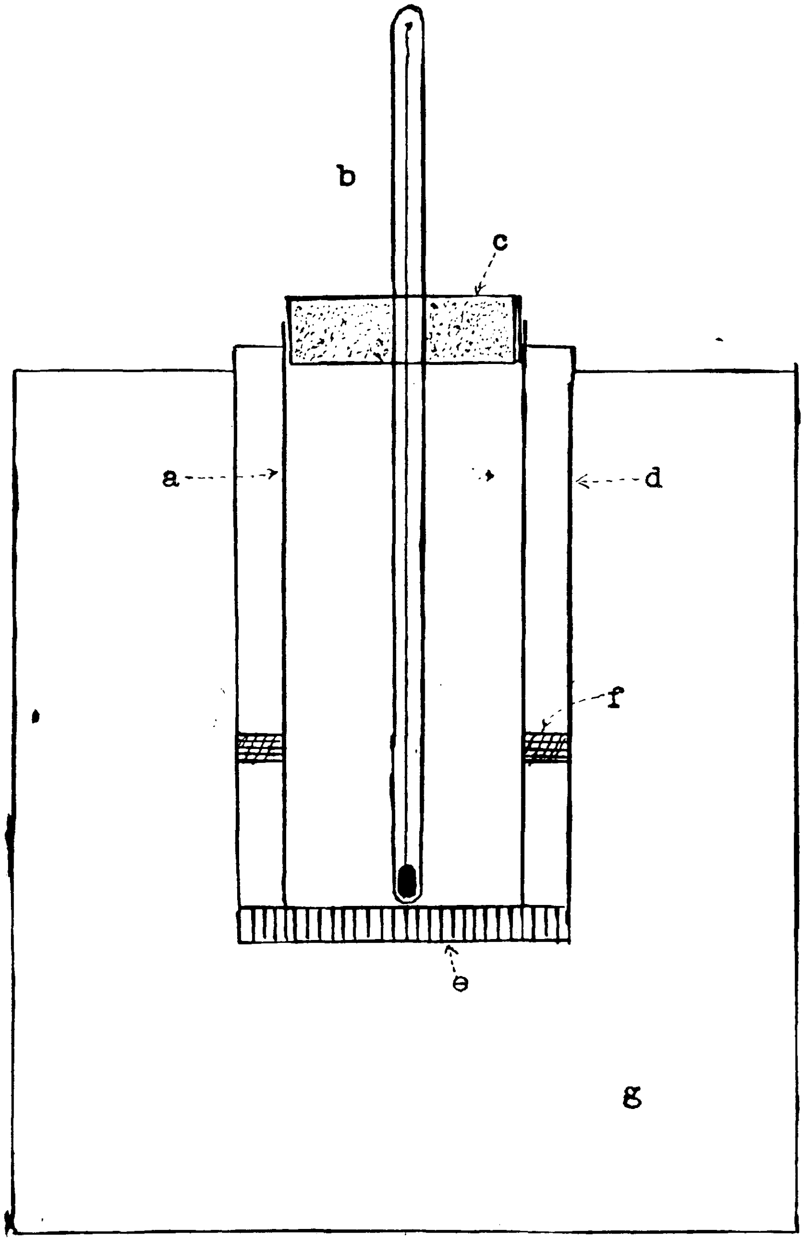


Fig. 1 - Apparatus for Cloud and Pour Test.

PROCEDURE

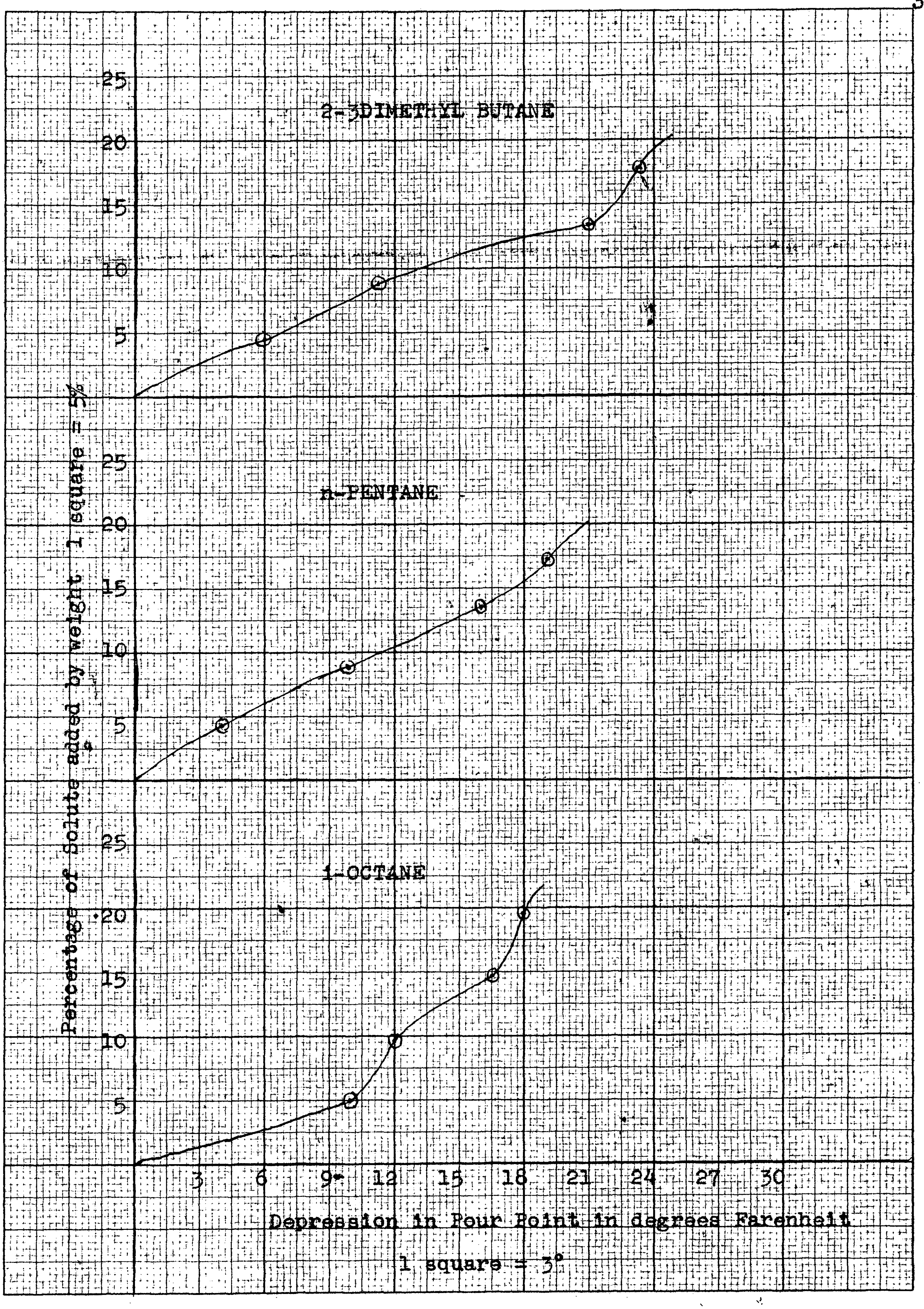
The procedure followed was closely related to the A.S.T.M. Pour Test. The wax sample was weighed accurately and melted in the test jar in a water bath. The jar was closed so that no water vapor would go into the sample. When the temperature of the melt came down to about 25^{o} higher than the melting point of the wax, the solute to be tested was added. The jar was then tightly closed by the cork carrying the thermometer. The disc was placed in the bottom of the jacket, and the test jar, with the ring gasket attached 1 in. above the bottom of the jar, was inserted into the jacket. When the temperature approached within 10^{o}F of the pour-point of the wax, the jar was taken out of the jacket and tilted just enough to ascertain whether there was any movement of the wax sample in the jar. The complete operation of removal and replacement of the jar was carried out in the prescribed time of 3 seconds. As soon as the wax sample ceased flowing when the test jar was tilted, the test jar was held in horizontal position for 5 seconds. When the wax sample was found not flowing, its temperature was taken as the pour-point with the stipulated correction of 5^{o}F. This procedure was repeated with equal increments of solute.

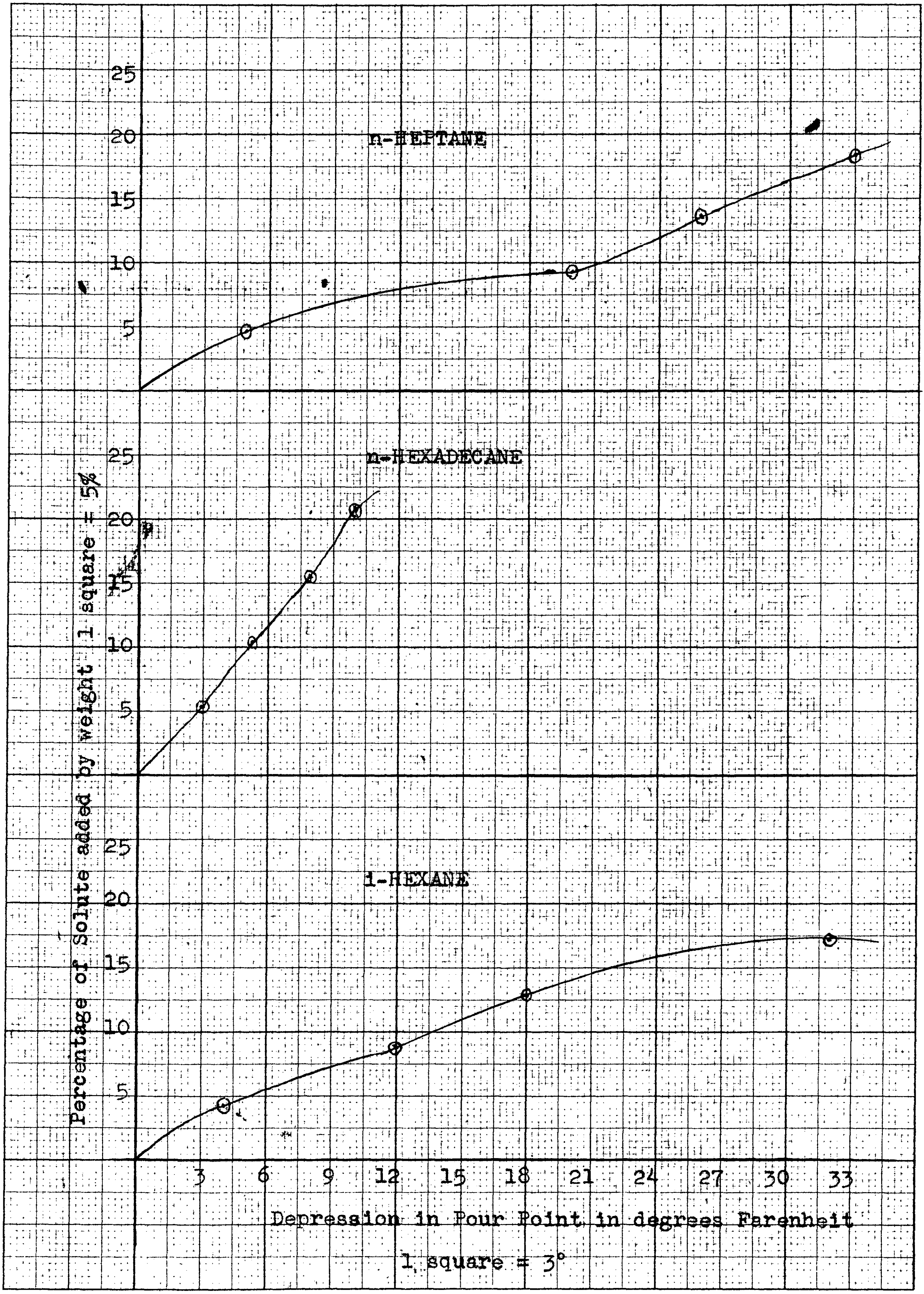
The various substances used in the investigation are listed in the tables that follow. The results of the tests are also included in the tables. The graphs illustrate the effect of the various substances.

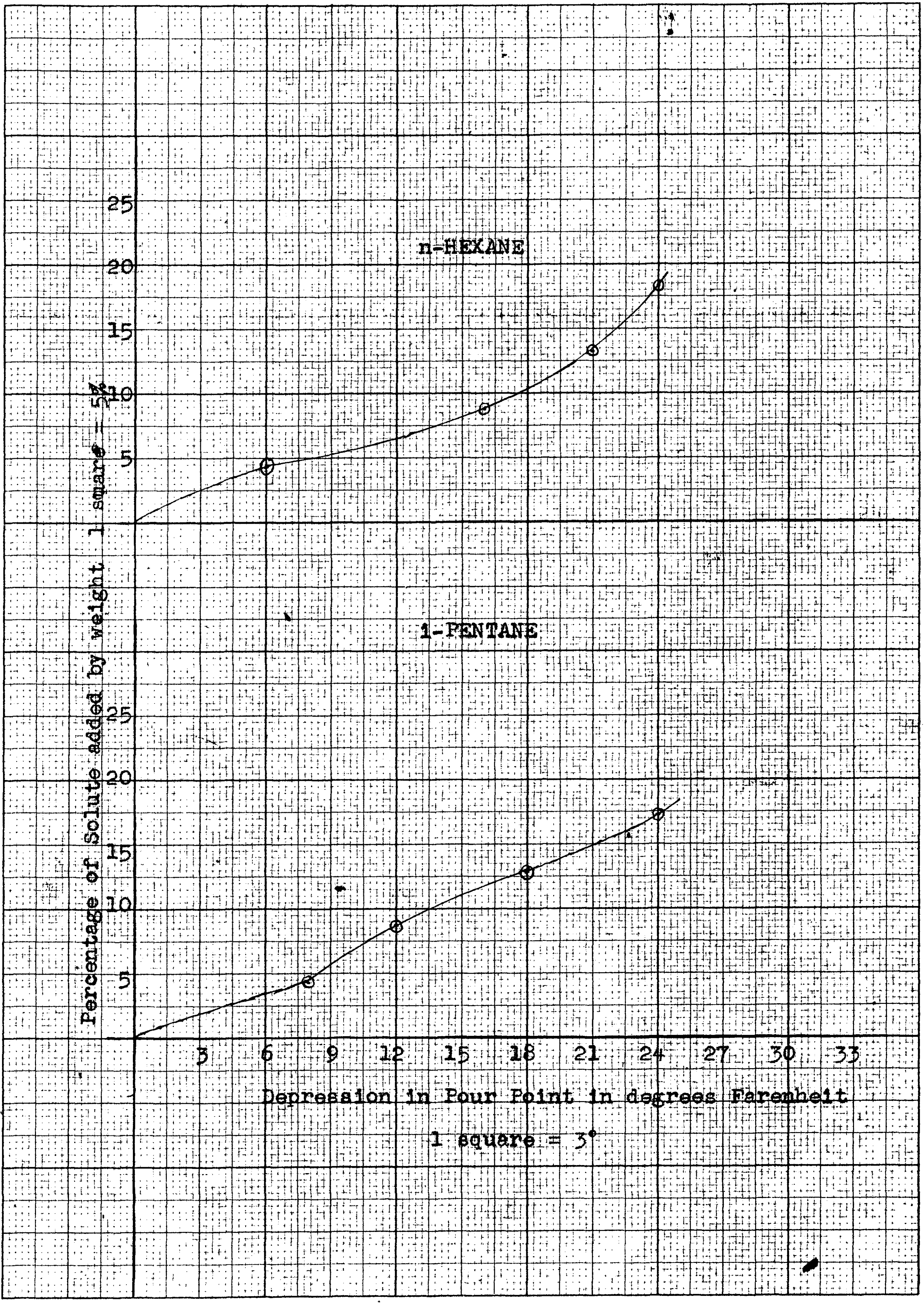
Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
2-3Dimethyl Butane 86.17 gm .668 gm/cc	1	.6680	4.45	15 gm	120°	6°
	2	1.3360	8.90	"	115°	11°
	3	2.0040	13.35	"	105°	21°
	4	2.6720	17.80	"	103°	23°
n-Pentane 72.15 gm .626 gm/cc	1	.626	4.42	14.1930	122°	4°
	2	1.252	8.84	"	116°	10°
	3	1.878	13.26	"	110°	16°
	4	2.504	17.68	"	107°	19°
1-Octane 114.23 gm .7029 gm/cc	1	.7029	4.88	14.3806	116°	10°
	2	1.4058	9.76	"	114°	12°
	3	2.1087	14.64	"	111°	15°
	4	2.8116	19.52	"	108°	18°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
n-Heptane 0.68376 gm/cc	1	0.68376	4.55	15.00 gm	121°	5°
	2	1.36752	9.10	"	106°	20°
	3	2.05128	13.65	"	100°	26°
	4	2.73504	18.20	"	93°	33°
n-Hexadecane .7751 gm/cc Mol. Wt. 226	1	.7751	5.2	14.9437 gm	123°	3°
	2	1.550	10.4	"	121°	5°
	3	2.3250	15.6	"	118°	8°
	4	3.1000	20.8	"	116°	10°
i-Hexane .6503 Mol. Wt. 86.17	1	.6503	4.33	15.0130 gm	122°	4°
	2	1.3006	8.66	"	114°	12°
	3	1.9509	12.99	"	108°	18°
	4	2.6012	17.32	"	94°	32°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
n-Hexane .6603 gm/cc Mol. Wt. 86.17	1	.6603	4.35	15.191 gm	120°	6°
	2	1.3206	8.70	"	110°	16°
	3	1.9809	13.05	"	105°	21°
	4	2.6412	18.4	"	102°	24°
i-Pentane 72.15 .6210 gm/cc	1	.6210	4.32	14.010 gm	118°	8°
	2	1.2420	8.64	"	114°	12°
	3	1.8630	12.96	"	108°	18°
	4	2.4840	17.28	"	102°	24°

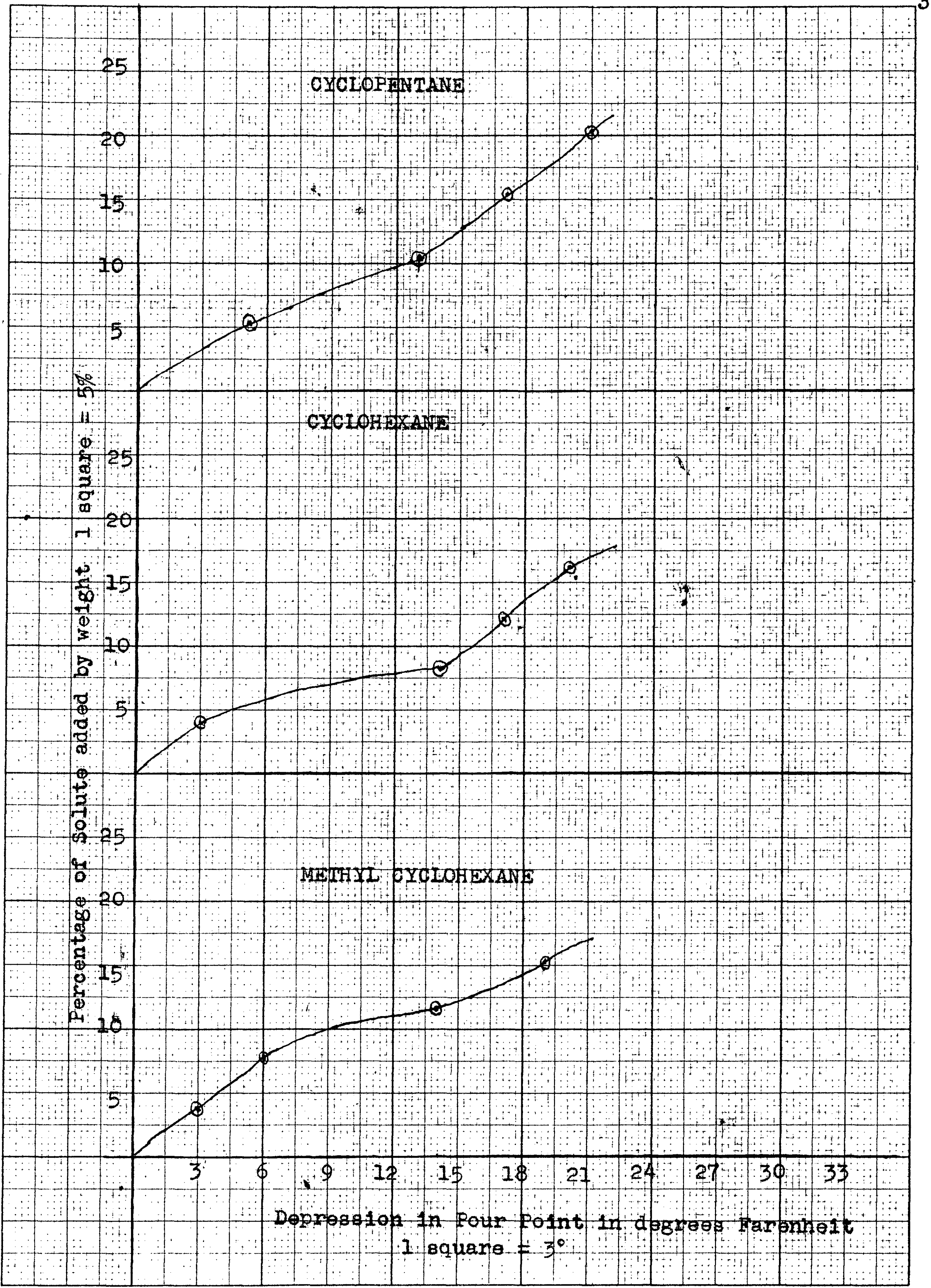

2-3DIMETHYL BUTANE
n-PENTANE
1-OCTANE
25
20
15
10
5
Percentage of Solute added by weight 1 square = 5%
3
6
9
12
15
18
21
24
27
30
Depression in Pour Point in degrees Farenheit
1 square = 3°

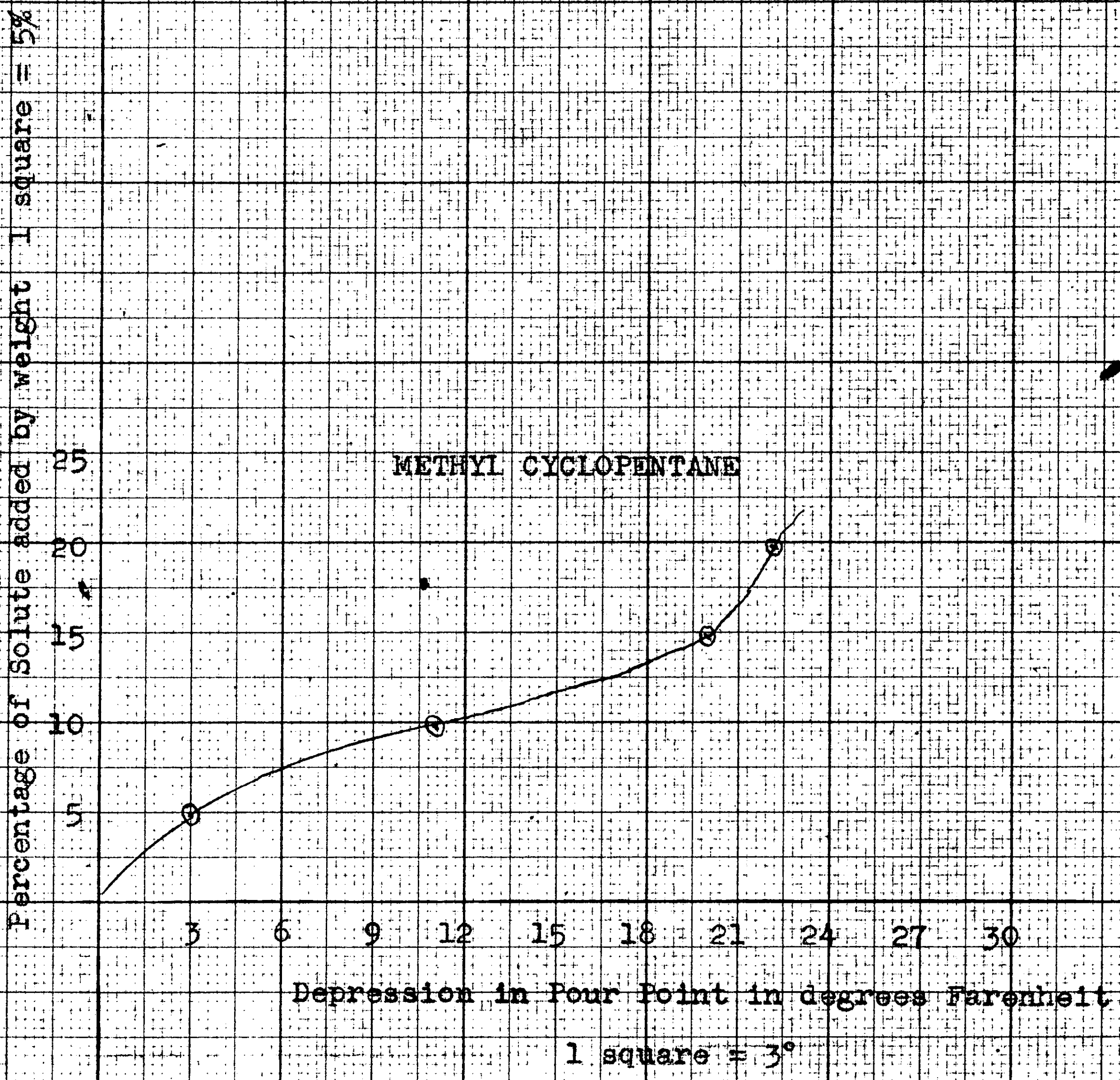

n-HEPTANE
n-HEXADECANE
1-HEXANE
25
20
15
10
5
25
20
15
10
5
25
20
15
10
5
3
6
9
12
15
18
21
24
27
30
33
Percentage of Solute added by weight 1 square = 5%
Depression in Pour Point in degrees Farenheit
1 square = 3°


n-HEXANE
1-PENTANE
25
20
15
10
5
Percentage of Solute added by weight 1 square = 5%
3
6
9
12
15
18
21
24
27
30
33
Depression in Pour Point in degrees Farenheit
1 square = 3°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Cyclopentane	1	.7510	5.1	14.7611 gm	121°	5°
Mol. Wt. 70.13 .7510 gm/cc	2	1.5070	10.2	" "	113°	13°
	3	2.2530	15.3	" "	109°	17°
	4	3.0040	20.4	" "	105°	21°
Cyclohexane	1	.7791	4.02	" "	123°	3°
Mol.Wt. 84.16 .7791 gm/cc	2	1.5582	8.04	" "	112°	14°
	3	2.3373	12.06	" "	109°	17°
	4	3.1164	16.08	" "	106°	20°
Methyl Cyclo-hexane	1	.7864	3.84	20.4161 gm	123°	3°
98.18 .7864 gm/cc	2	1.5728	7.68	" "	120°	6°
	3	2.3592	11.52	" "	112°	14°
	4	3.1456	15.36	" "	107°	19°

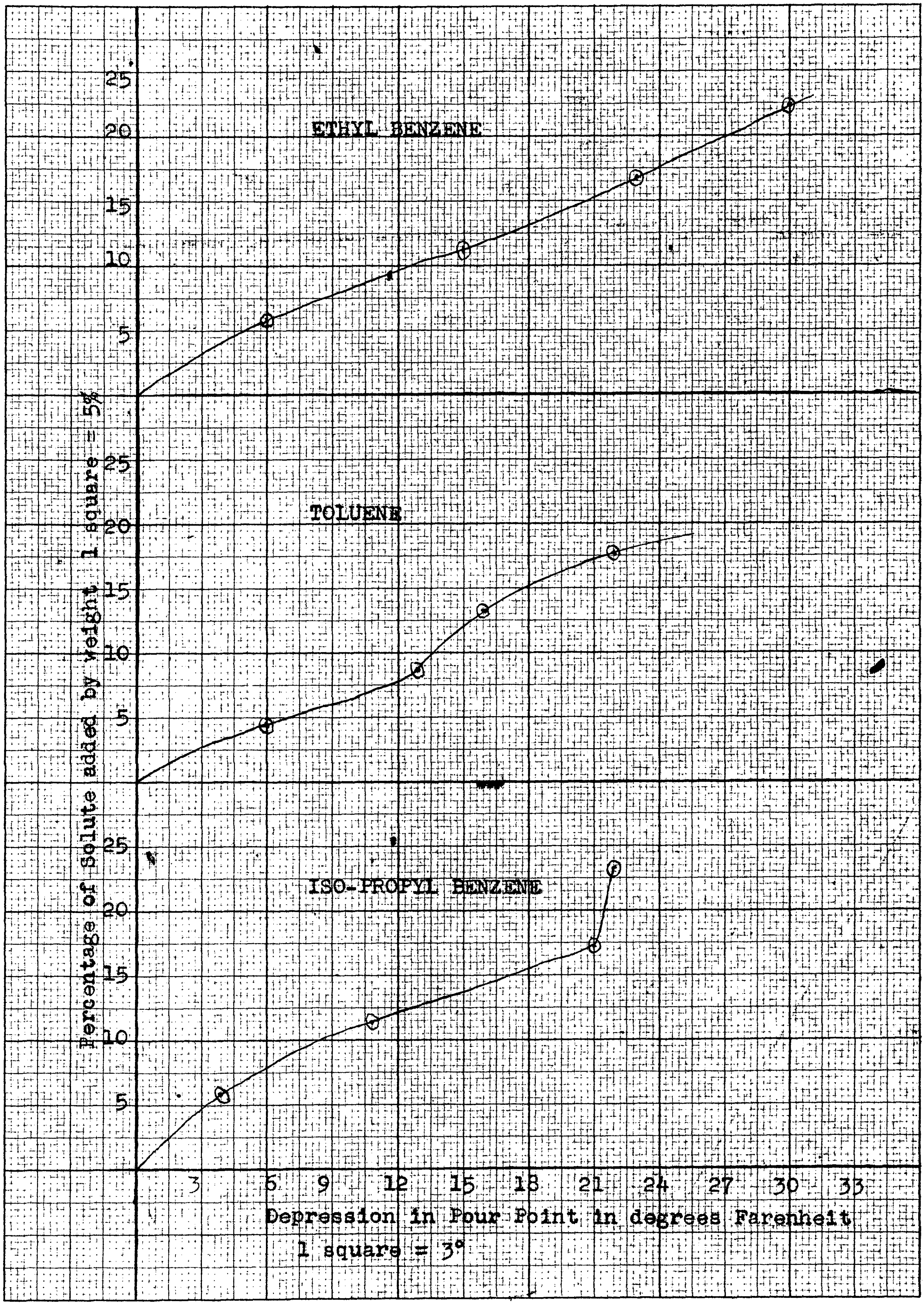
Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Methyl Cyclopentane .7566 gm/cc Mol.Wt. 84.16	1	.7566	4.92	15.3637 gm	123°	3°
	2	1.5132	9.84	"	115°	11°
	3	2.2698	14.76	"	106°	20°
	4	3.0264	19.68	"	104°	22°

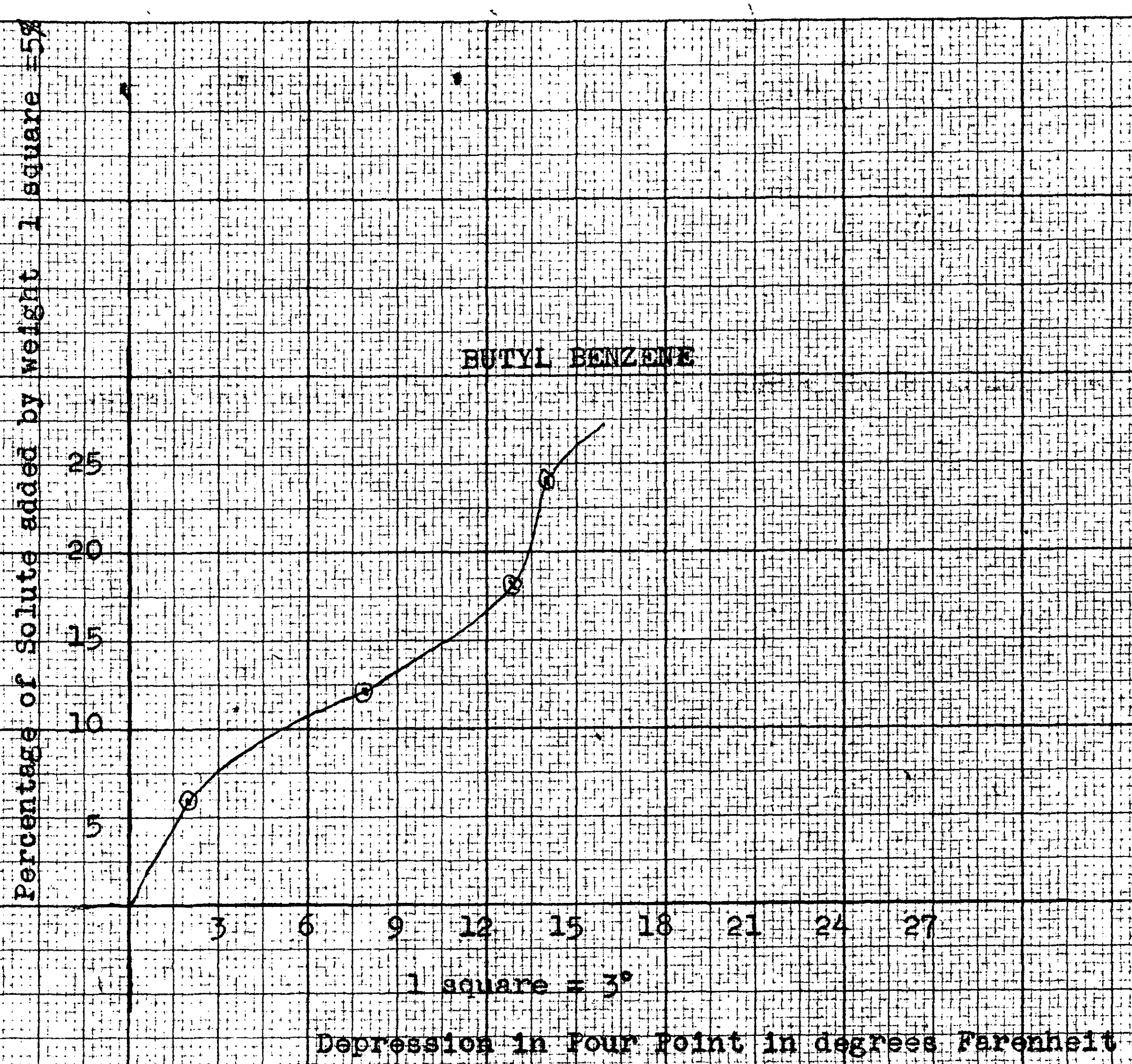

CYCLOPENTANE
CYCLOHEXANE
METHYL CYCLOHEXANE
Percentage of Solute added by weight 1 square = 5%
25
20
15
10
5
3
6
9
12
15
18
21
24
27
30
33
Depression in Pour Point in degrees Farenheit
1 square = 3°


METHYL CYCLOPENTANE
Percentage of Solute added by weight 1 square = 5%
25
20
15
10
5
3
6
9
12
15
18
21
24
27
30
Depression in Pour Point in degrees Farenheit
1 square = 3°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Iso-Propyl Benzene	1	.86179	5.72	15.040 gm	122°	4°
Mol.Wt. 120.19 .86179 gm/cc	2	1.72358	11.44	"	115°	11°
	3	2.58537	17.16	"	105°	21°
	4	3.44716	22.88	"	104°	22°
Toluene	1	.86694	4.4	19.7129 gm	120°	6°
Mol.Wt. 92.13 .86694 gm/cc	2	1.73388	8.8	"	113°	13°
	3	2.60082	13.2	"	110°	16°
	4	3.46776	17.6	"	104°	22°
Ethyl Benzene	1	.8669	5.53	15.6671 gm	120°	6°
Mol.Wt. 106.16 .8669 gm/cc	2	1.7338	11.06	"	111°	15°
	3	2.6007	16.59	"	103°	23°
	4	3.4676	22.12	"	96°	30°

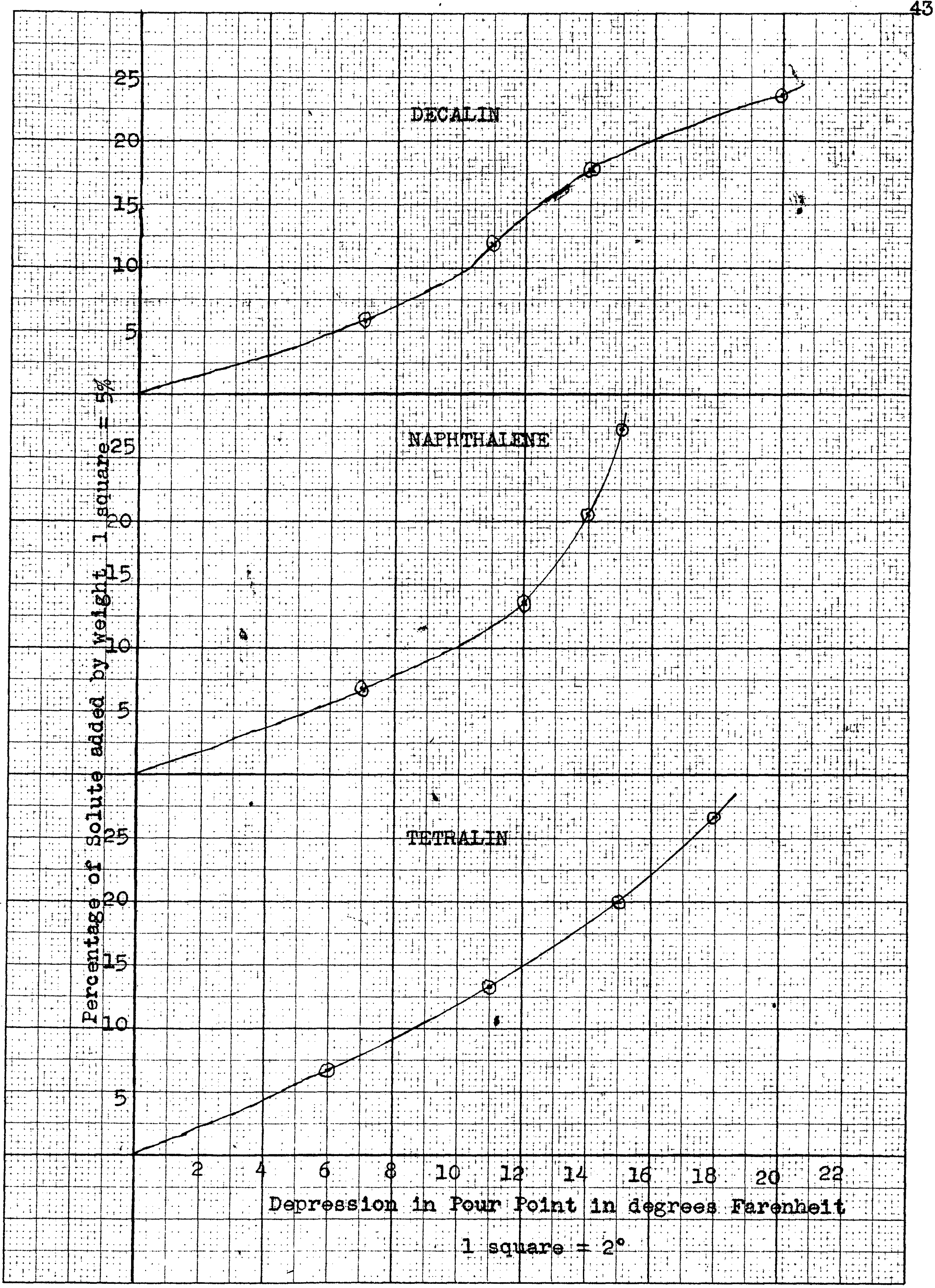
Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Butyl Benzene	1	.86013	6	14.3692 gm	124°	2°
Mol. Wt. 134.21 .86013 gm/cc	2	1.72026	12	"	118°	8°
	3	2.58039	18	"	113°	13°
	4	3.4452	24	"	112°	14°

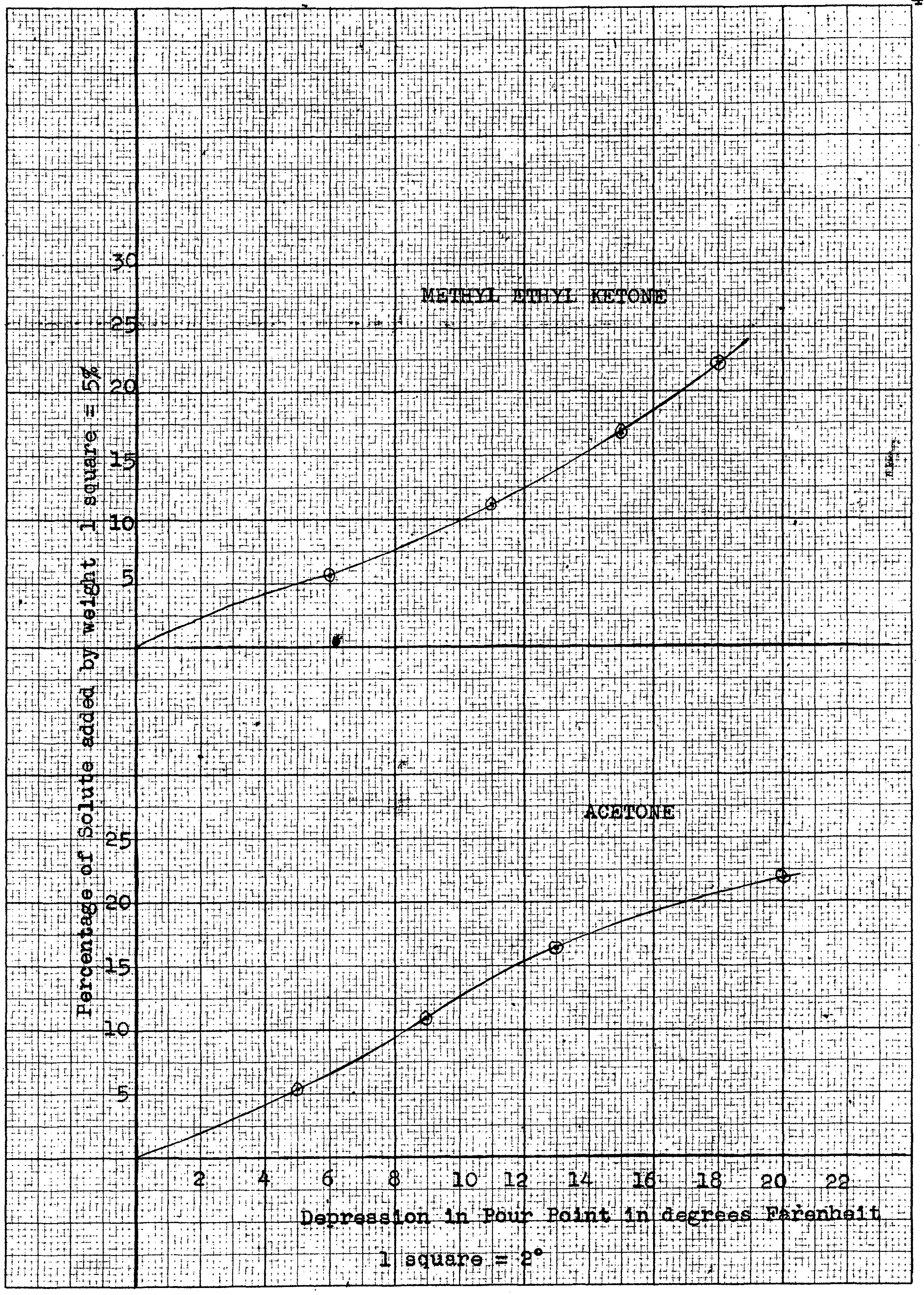

ETHYL BENZENE
TOLUENE
ISO-PROPYL BENZENE
25
20
15
10
5
Percentage of Solute added by Weight 1 square = 5%
3
6
9
12
15
18
21
24
27
30
33
Depression in Pour Point in degrees Farenheit
1 square = 3°


BUTYL BENZENE
Percentage of Solute added by weight 1 square =5%
5
10
15
20
25
3
6
9
12
15
18
21
24
27
1 square = 3°
Depression in Pour Point in degrees Farenheit

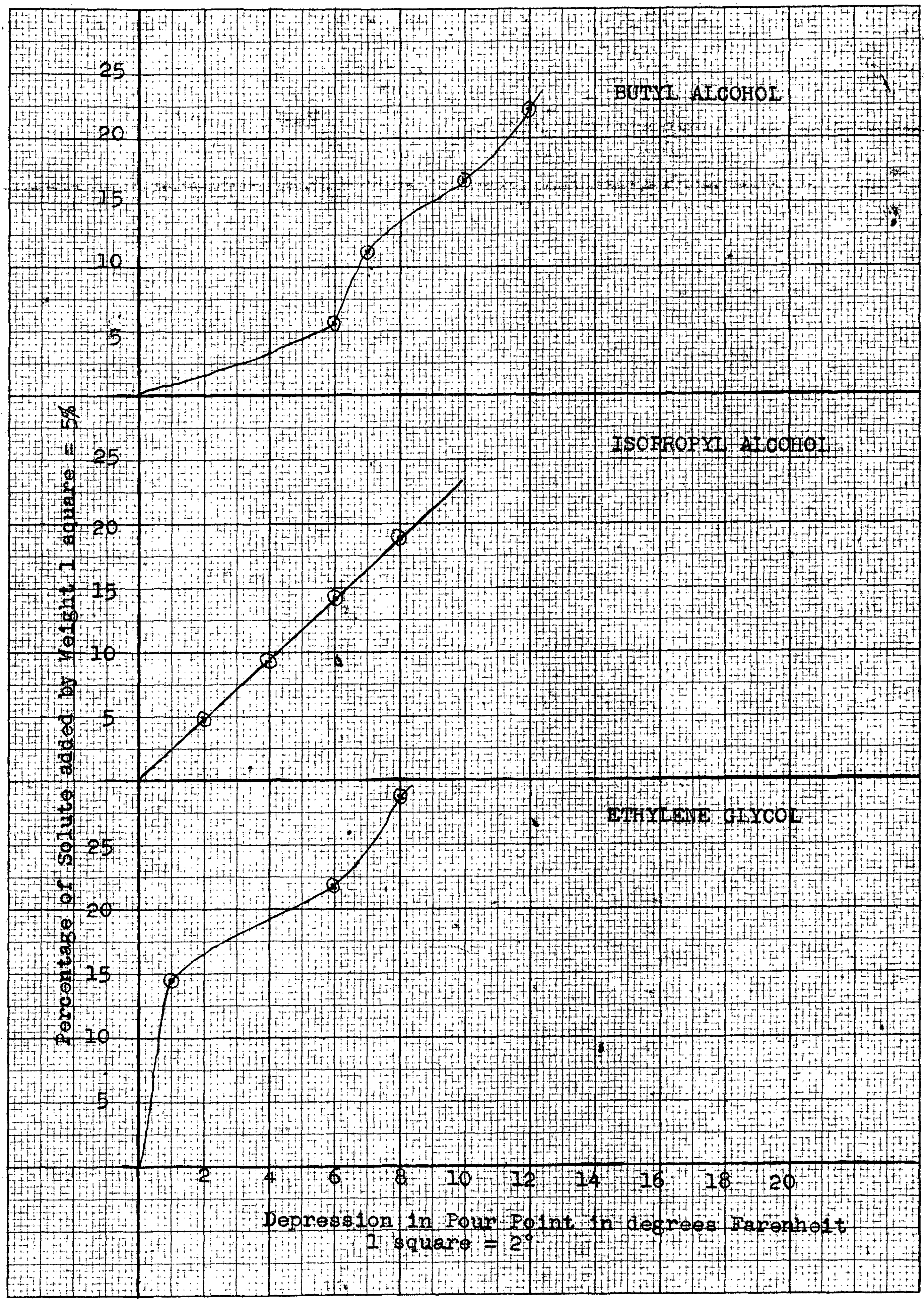
Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Decalin Mol.Wt. 138.25 .8963 gm/cc	1	.8963	5.92	15.1291 gm	119°	7°
	2	1.7926	11.84	"	115°	11°
	3	2.6889	17.76	"	112°	14°
	4	3.5852	23.68	"	106°	20°
Naphthalene Mol.Wt. 128.16 1.145 gm/cc	1		6.83	14.6379 gm	119°	7°
	2		13.66	"	114°	12°
	3		20.49	"	112°	14°
	4		27.32	"	111°	15°
Tetralin Mol.Wt. 132.20 .971 gm/cc	1	.971	6.66	14.5831 gm	120°	6°
	2	1.942	13.32	"	115°	11°
	3	2.913	19.98	"	111°	15°
	4	3.884	26.64	"	108°	18°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Methyl Ethyl Ketone .805 gm/cc Mol.Wt. 72.10	1	.805	5.57	14.4502 gm	120°	6°
	2	1.610	11.14	"	115°	11°
	3	2.415	16.71	"	111°	15°
	4	3.220	22.28	"	108°	18°
Acetone Mol.Wt. 58.8 .792 gm/cc	1	.792	5.45	14.5695 gm	121°	5°
	2	1.584	10.90	"	117°	9°
	3	2.376	16.35	"	113°	13°
	4	3.168	21.80	"	106°	20°


DECALIN
NAPHTHALENE
TETRALIN
Percentage of Solute added by weight 1 square = 5%
25
20
15
10
5
25
20
15
10
5
25
20
15
10
5
2
4
6
8
10
12
14
16
18
20
22
Depression in Pour Point in degrees Farenheit
1 square = 2°

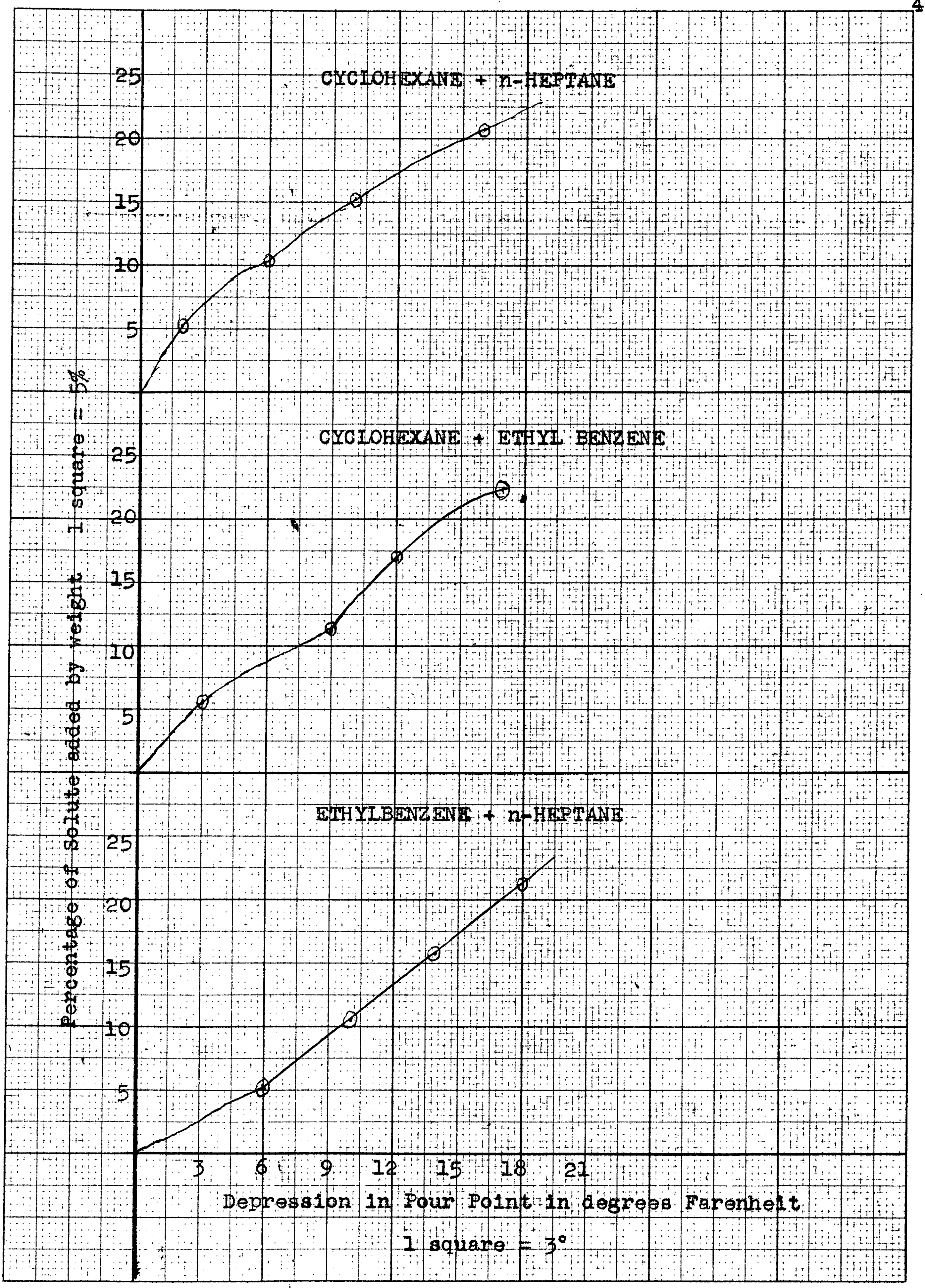

METHYL ETHYL KETONE
30
25
20
15
10
5
ACETONE
25
20
15
10
5
Percentage of Solute added by weight 1 square = 5%
2
4
6
8
10
12
14
16
18
20
22
Depression in Pour Point in degrees Farenheit
1 square = 2°

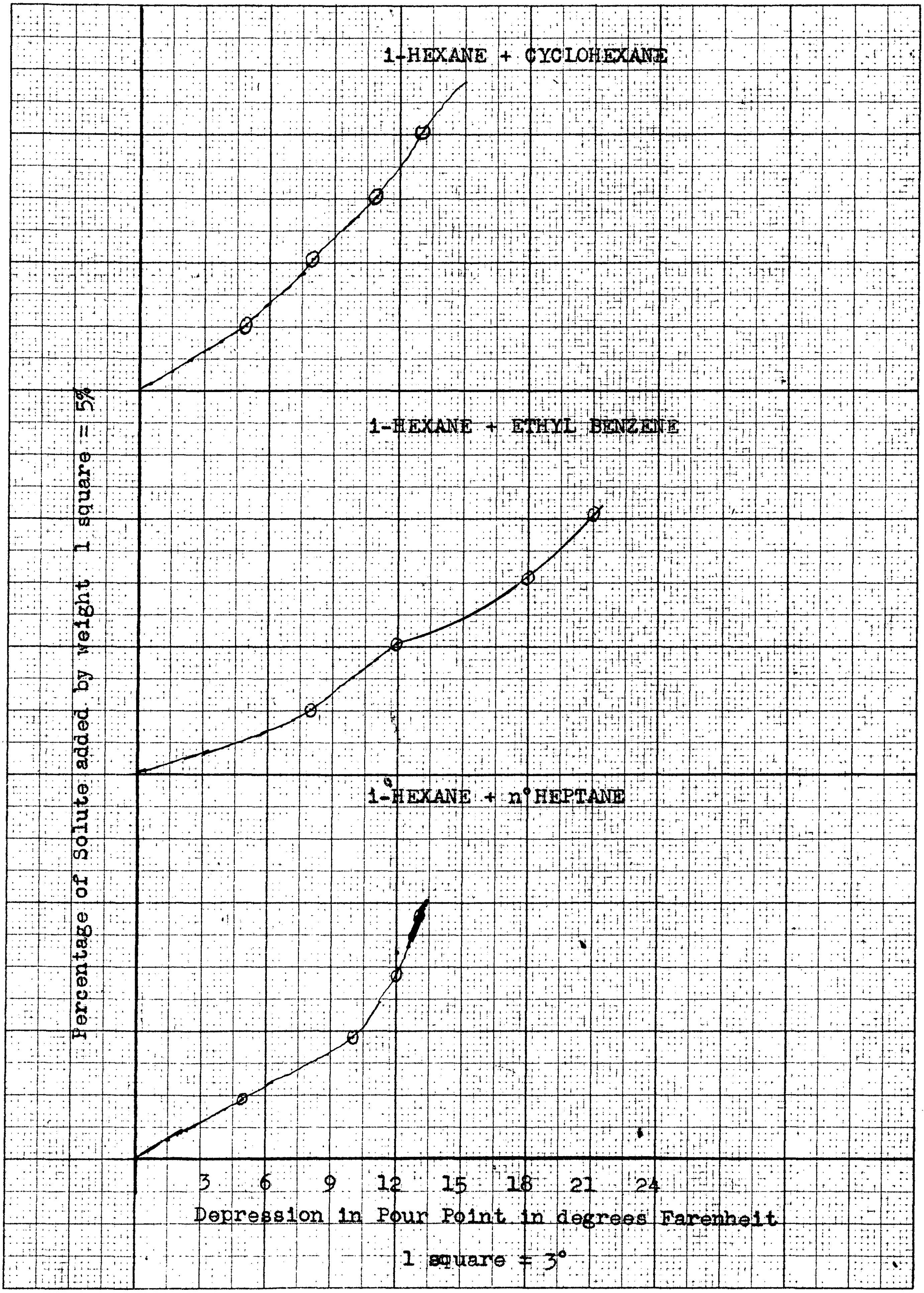
Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Butyl Alcohol Mol. Wt.74.12 .80978 gm/cc	1	.80978	5.52	14.670 gm	120°	6°
	2	1.61956	11.04	"	119°	7°
	3	2.42934	16.56	"	116°	10°
	4	3.23912	22.08	"	114°	12°
Isopropyl Alcohol Mol.Wt. 60.09 .7854 gm/cc	1	.7854	4.7	16.314 gm	124°	2°
	2	1.5708	9.4	"	122°	4°
	3	2.3562	14.1	"	120°	6°
	4	3.1416	18.8	"	118°	8°
Ethylene Glycol Mol.Wt. 62.07 1.1155 gm/cc	1	1.1155	7.24	15.421 gm	127°	1°
	2	2.2310	14.48	"	125°	-1°
	3	3.3465	21.72	"	120°	-6°
	4	4.4620	28.96	"	118°	-8°


BUTYL ALCOHOL
ISOPROPYL ALCOHOL
ETHYLENE GLYCOL
25
20
15
10
5
Percentage of Solute added by Weight 1 square = 5%
2
4
6
8
10
12
14
16
18
20
Depression in Pour Point in degrees Farenheit
1 square = 2°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
Cyclohexane n-Heptane	1	.7314	5.13	14.2723 gm	124°	2°
	2	1.4628	10.26	"	120°	6°
	3	2.1942	15.39	"	116°	10°
	4	2.9256	20.52	"	110°	16°
Cyclohexane Ethyl Benzene	1	.823	5.62	14.6272 gm	123°	3°
	2	1.646	11.22	"	117°	9°
	3	2.469	16.96	"	114°	12°
	4	3.292	22.48	"	109°	17°
Ethylbenzene n-Heptane	1	.7763	5.26	14.7372 gm	120°	6°
	2	1.5526	10.52	"	116°	10°
	3	2.3289	15.78	"	112°	14°
	4	3.3052	21.04	"	108°	18°

Solute	cc	Gm of Solute	% of Solute	Wt. of Wax	Observed Pour-Point	Difference
i-Hexane Cyclohexane	1	.7147	5.08	14.0805 gm	121°	8°
	2	1.4294	10.16	"	118°	8°
	3	2.1441	15.24	"	115°	11°
	4	2.8588	20.32	"	113°	13°
i-Hexane Ethyl Benzene	1	.7586	5.1	14.8239 gm	118°	8°
	2	1.5172	10.2	"	114°	12°
	3	2.3758	15.3	"	108°	18°
	4	3.1344	20.4	"	105°	21°
i-Hexane n Heptane	1	.667	4.75	14.0658 gm	121°	5°
	2	1.334	9.50	"	116°	10°
	3	2.001	14.25	"	114°	12°
	4	2.668	19.00	"	113°	13°

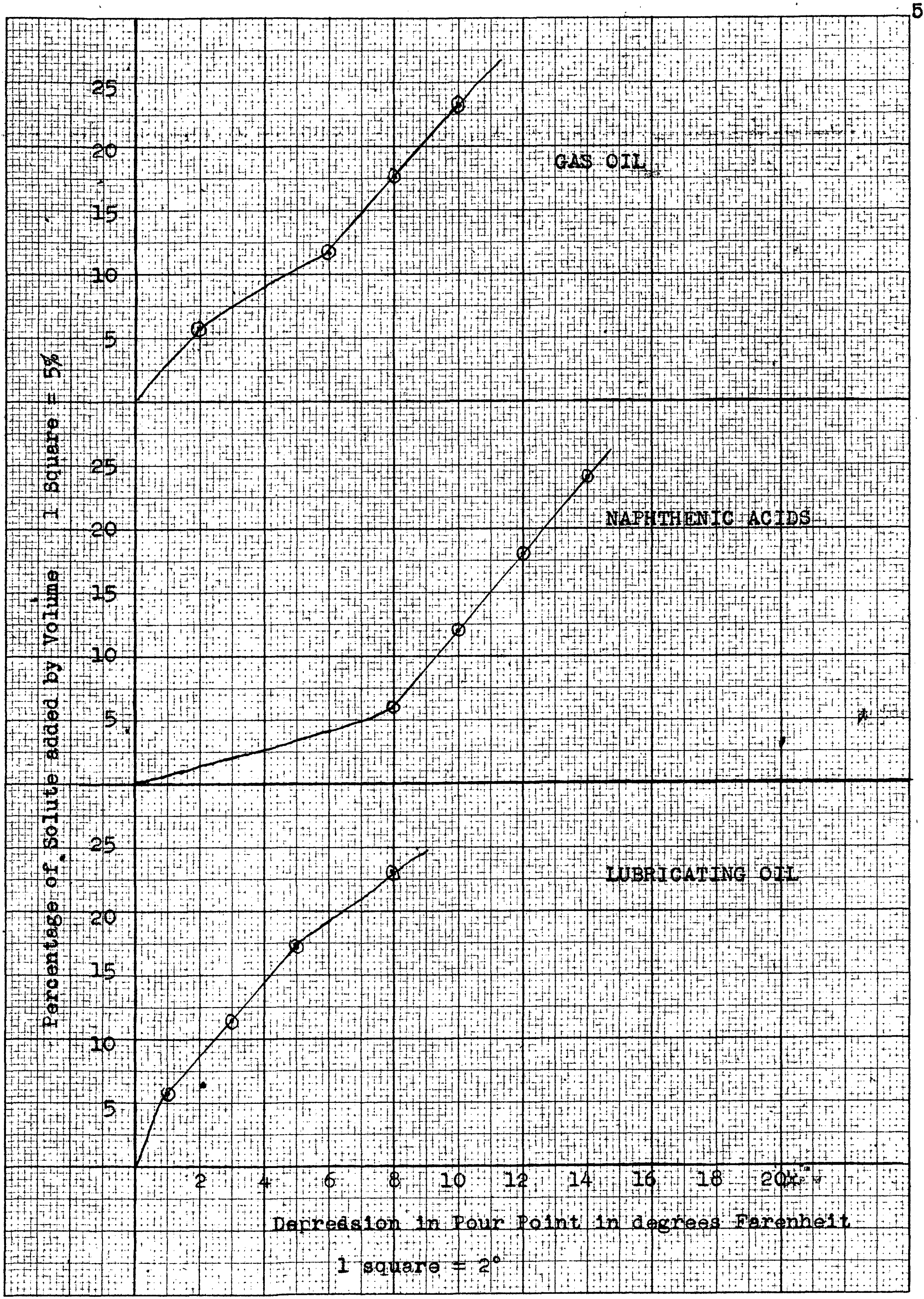

CYCLOHEXANE + n-HEPTANE
CYCLOHEXANE + ETHYL BENZENE
ETHYLBENZENE + n-HEPTANE
25
20
15
10
5
Percentage of Solute added by weight 1 square = 5%
3
6
9
12
15
18
21
Depression in Pour Point in degrees Farenheit
1 square = 3°

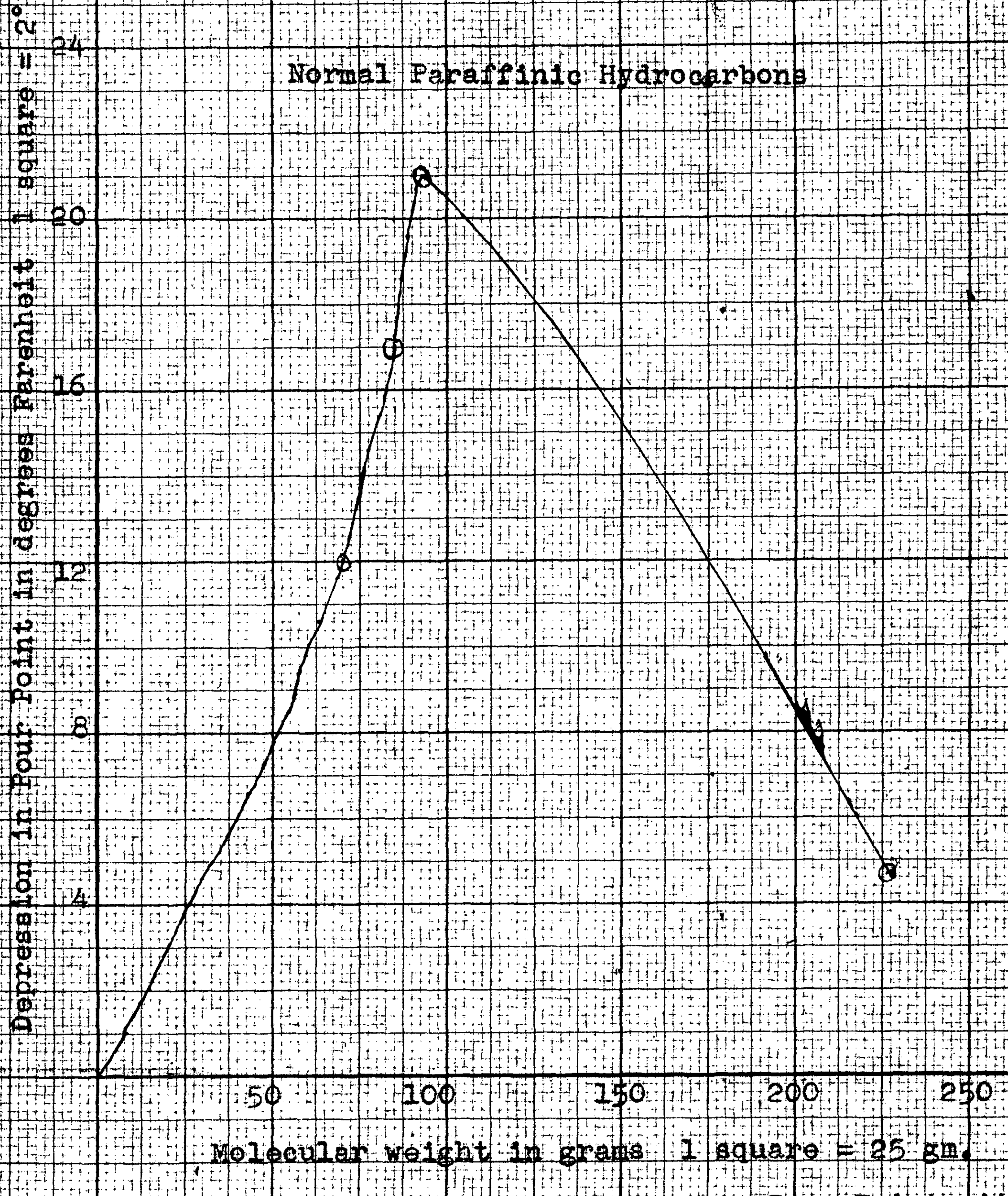

1-HEXANE + CYCLOHEXANE
1-HEXANE + ETHYL BENZENE
1-HEXANE + n°HEPTANE
Percentage of Solute added by weight 1 square = 5%
3
6
9
12
15
18
21
24
Depression in Pour Point in degrees Farenheit
1 square = 3°

The following class of compounds were found to be immiscible:

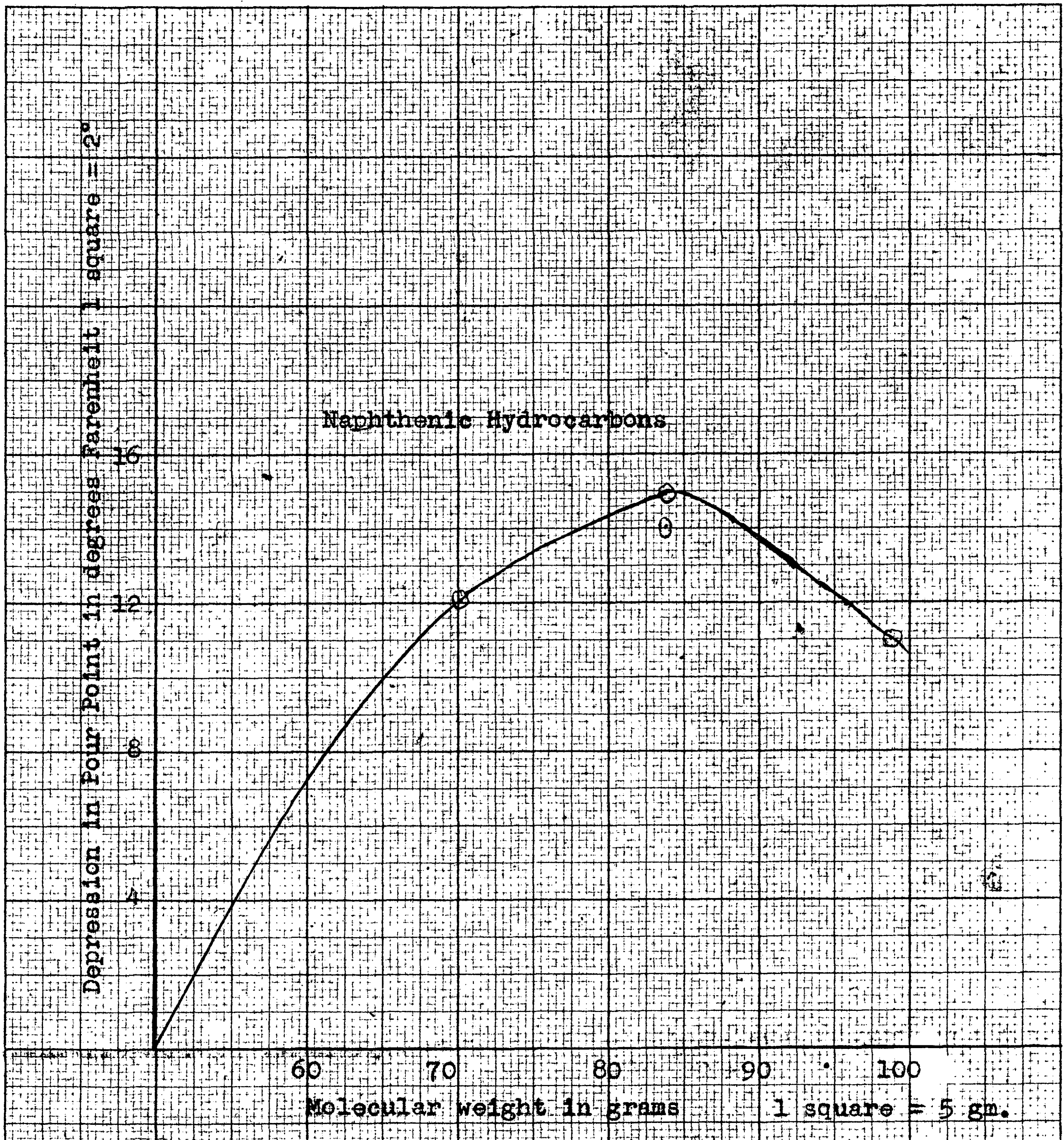
1. Trihydric alcohol such as glycerol
2. Sulphonates
3. Phenols
4. Nitrites
5. Nitrobenzene
6. Furfural

Solute	cc	% of Solute	Wt. and Vol. of Wax	Observed M. Pt.	Difference	
Gas Oil	1	5.85	14.4692 gm 17.10 cc	124°	2°	
	2	11.70		120°	6°	
	3	17.55		118°	8°	
	4	23.40		116°	10°	
Naphthenic Acids	1	6	14.0948 gm 16.65 cc	118°	8°	
	2	12		116°	10°	
	3	18		114°	12°	
	4	24		112°	14°	
Lubricating Oil	1	5.75	14.7140 gm 17.40 cc	125°	1°	
	2	11.50		123°	3°	
	3	17.25		121°	5°	
	4	23.00		118°	8°	

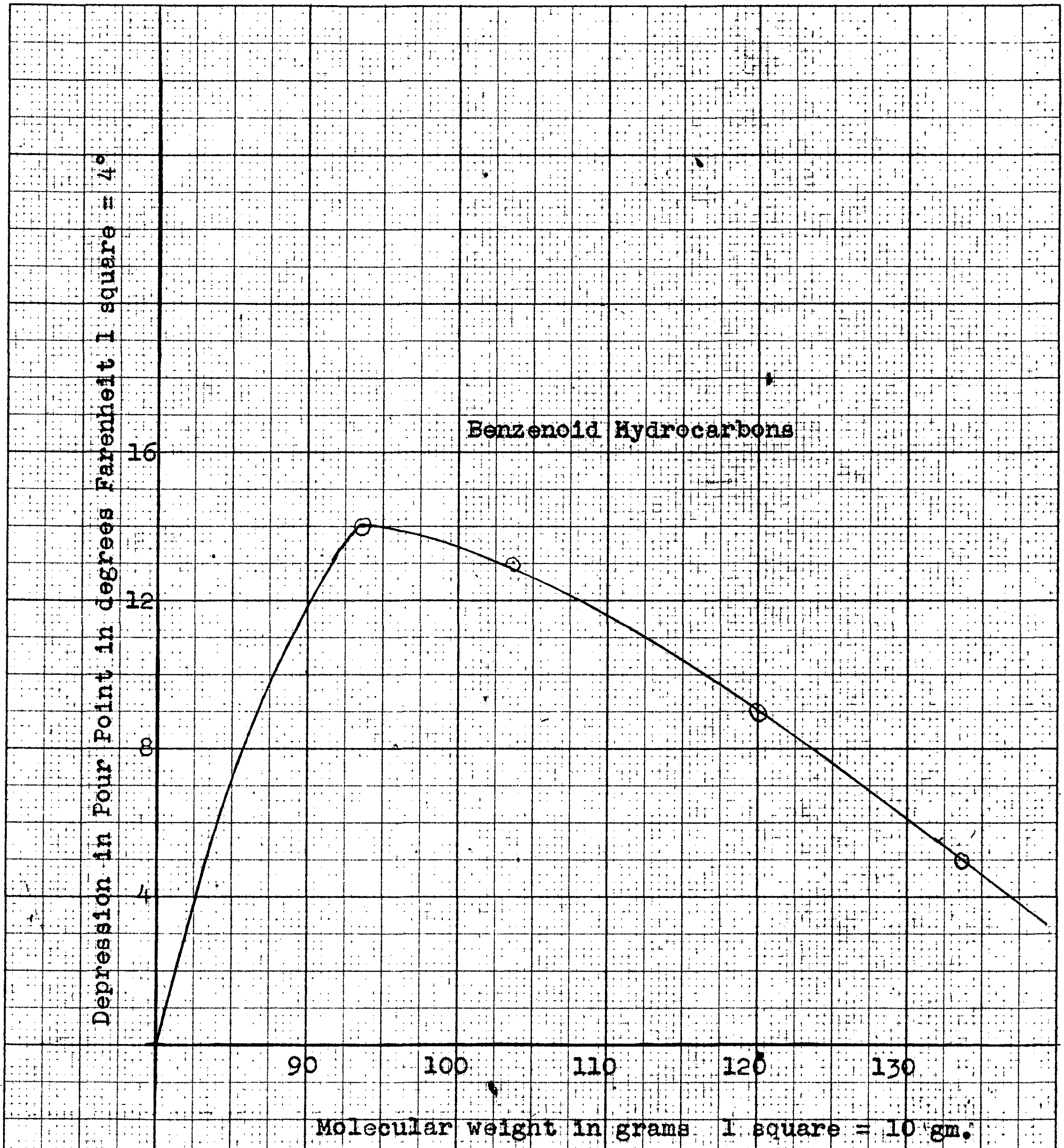

GAS OIL
NAPHTHENIC ACIDS
LUBRICATING OIL
25
20
15
10
5
Percentage of Solute added by Volume 1 Square = 5%
2
4
6
8
10
12
14
16
18
20
Depression in Pour Point in degrees Farenheit
1 square = 2°



Graph showing the depression in Pour Point with 10% addition of Solute



Graph showing the depression in Pour Point with 10% addition of Solute



Graph showing the depression in Pour Point with 10% addition of Solute

CONCLUSIONS

At the end of all the tests the results were plotted as percentages of solute added to the wax sample against the lowering in degrees of pour-point. Almost all the substances added tended to show a lowering in the pour-point. But all were not uniform in their behavior. This behavior can be analyzed from the point of view of the class of compounds to which they belong.

Paraffins, as a class, whether normal or branched-chain, tended to show a marked lowering of pour-point. The compound which exhibited this tendency the most were normal heptane and isohexane. Benzenoid derivatives, especially ethylbenzene, were also quite effective in lowering the pour-points. Naphthenic derivatives were moderate in their effect on lowering of pour-point. Naphthalene derivatives were found to be not much better than benzenoid derivatives in this respect.

A very interesting peculiarity was observed in curves plotting molecular weights against the depression in pour-point with a definite quantity of the solute. The curves rise with increase in molecular weight, reach a peak, and then begin to descend with further increase in molecular weight. Interpretation of the latter part of the curve is understandable, as the freezing point of the higher-molecular-weight compounds increases with the increase in molecular weight. But the interpretation of the first part is rather obscure. This behavior is marked in all classes of compounds.

The expectation that the addition of solids would produce a behavior pattern similar to that of metallic alloys was not fulfilled. Even though the pour-point was lowered, the lowering was not so pronounced as to warrant an assumption that the behavior of solids is similar to that of fusible alloys.

Not much can be said about the effect of the molecular structures; any conclusion drawn would be hazardous, because the number of compounds tried was insufficient to be completely representative of the different classes. But without being committed to any definite statements, the author can say that the paraffin hydrocarbons were more effective than any other class of compounds in lowering the pour-point.

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