

THE DENSITIES AND COOLING CURVES
OF
MICROCRYSTALLINE WAXES

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OF
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BY

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STRATHMORE PARCHMENT

PREFACE

This thesis is based upon work done as incumbent under Bareco Project Number 2, a research project set up in the Engineering Experiment Station of Oklahoma Agricultural and Mechanical College by the Bareco Oil Company of Barnsdall, Oklahoma, on August 1, 1944. This work was done under the direction of Dr. H. M. Trimble of the Department of Physical Chemistry.

TABLE OF CONTENTS

	Page
Introduction	1
Preliminary Considerations	9
Experimental Work	24
Conclusions	35
Bibliography	37
Autobiography	39

INTRODUCTION

As early as 1838, Balozieski (89) gave the first suggestion of a distinction between types of petroleum waxes. He stated that isoparaffins, "protoparaffin" (the progenitor of paraffin waxes), of high molecular weight were not themselves crystallizable. These yielded well-crystallized, normal, low-molecular-weight paraffins, "pyroparaffin", on dry distillation or pyrolysis. He believed that waxes of high molecular weight in petroleum, separated first from crude oils as rosin wax, consisted largely of isoparaffins. In agreement with the trend of modern theory, he believed that crystalline and amorphous forms of wax existing as colloidal jelly were present in petroleum.

The earliest work done on American petroleum waxes was conducted by Hebery (17). Using an homologous series of hydrocarbons, he found the first paraffin solid to be $C_{15}H_{32}$, melting at $10^{\circ}C$. In commercial wax the lowest molecular weight hydrocarbon was $C_{22}H_{44}$, melting at $48^{\circ}C$. He isolated six fractions which were twenty-one per cent of the original material. He thought them to be pure normal compounds. His list includes waxes up to $C_{31}H_{62}$ with melting-points of $76-77^{\circ}C$. He concluded that ordinary paraffins, normal hydrocarbons, fall within the range of $C_{22}H_{44}$ to $C_{29}H_{58}$. He also gave some consideration to the structure of high-boiling, high-molecular-weight soft waxes in petroleum. He couldn't differentiate between these waxes, but the isolations he made of the fairly pure paraffins were of importance.

Krafft (15, 16) in 1907 produced a series of synthetic paraffins and stated their properties. It is doubtful if he isolated pure

compounds. It remained for Marcusson (13) in 1914 to show that ceresins and well-crystallized paraffins of about the same melting-point have different molecular weights and different chemical and physical properties, particularly specific gravity and refractive index. Therefore, he deduced the possibility of a branched structure in ceresins.

From Scotch shale oil, Francis and his co-workers (8, 9) obtained twenty-one separate wax fractions from high-vacuum distillations. These rather pure products had the properties of synthetic paraffins and accounted for a high percentage of his samples. Possibly seven or eight out of these fractions were pure. Piper and his workers (21) made x-ray investigations of Francis' fractions and confirmed Francis' determinations of molecular weights and of the number of carbon atoms present. Most important was the conclusion that there were some impurities in the pure individual normal paraffins but there were absolutely no isoparaffins in paraffin wax. In a later paper, Francis, Piper, and Halkin (10) found that long-chain paraffins occurring in nature are ~~always mixed~~ ^{mixtures} and consist, so far as they have been identified, of those containing odd numbers of carbon atoms only.

Perhaps the most comprehensive study of properties of waxes was made by Carpenter (4). He obtained hydrocarbons from $C_{21}H_{44}$ to $C_{34}H_{70}$ from pipe lines. One compound, $C_{27}H_{54}$, melting at $96.5^{\circ}C.$, was found. Successive fractions often had the same sharp melting-points but different molecular weights. Waxes from tank bottoms gave relatively high melting-point values. These high-melting-point waxes are comparatively insoluble in solvents and hard to purify to constant values for physical properties. As a result of his experiments with waxes from oils from Burma, Assam, the Dutch East Indies and America, Carpenter stated that

crystalline waxes are non-lubricious and can be formed by chemical changes, for example, by cracking, of amorphous wax or petroleum jelly.

Curwitsch (12), in his proposed structure of microcrystalline wax, concluded that amorphous paraffins differ from crystalline only in the size of the crystals, and the cause of the difference should be looked for in conditions (the viscosity of the medium from which they separate) which retard their crystallization. He demonstrated the presence of microcrystalline wax in petrolatum and said that no true colloidal jelly existed in such material.

"Soft" was the name given by Buchler and Graves (8) to soluble impurities in waxes. These "soft" waxes were supposed to be responsible for the formation of needle crystals in impure waxes and the formation of needle crystals in impure waxes and the formation of vaselines when high-melting waxes were mixed with oil. When the impurities were removed by drastic purification, the remaining fractions were found to belong to one series of homologous compounds. By comparison of properties, Buchler and Graves concluded that they had normal paraffins, but they failed to note the possibilities of branched-chain paraffins in their high-melting-point hydrocarbons. However, Buchler and Graves' methods of separation and their photomicrographs of plate-like crystals are pertinent material.

Sachonen, Zherdeva, and Vasilyov (23) worked with paraffin wax and so-called ceresins determining properties and structures. They defined these waxes as, respectively, "solid hydrocarbons derived from petroleum which could be removed in filter presses and vacated", and "hydrocarbons without these characteristics". Because of different physical properties: high molecular weight, retention of oil (which property can be

conferred upon paraffins), very high boiling-points, low vapor pressure, and delicate needle or short plate crystal structure (as revealed by photomicrographs), they stated that microcrystalline waxes are probably not normal paraffins.

Ferris, Henderson, and Cowles (7) prepared waxes having a wide range of melting-points and different from the usual "crystalline" wax. These waxes had higher boiling-points, finer crystalline texture, greater toughness, higher refractive indices, and higher molecular weights than did paraffin waxes. By dissolving and chilling in ethylene chloride, these compounds, consisting mainly of branched-chain paraffins and some cyclic unsaturated compounds, were prepared. Six fractions of high purity, proved by flat cooling curves, were obtained. Ferris, Henderson, and Cowles recognized a distinct series of waxes of decreasing melting-point for a given molecular weight and showed the presence of plate, microcrystalline, and needle forms. The needle forms were more soluble than the plates for a given molecular weight. Also they concluded that higher-boiling fractions carry poorly crystalline or non-crystalline material which imposes its characteristics on the otherwise suitable plate or needle wax. This brought out the nature of Buchler and Graves' "impurities".

Working with the waxes prepared by Ferris, Henderson, and Cowles, Clark and Smith (8, 9) employed their x-ray technique to show that there was a variability in diffraction spacings when the cooling time through the melting-point range of paraffin waxes varied. They showed that the spacing was a function of melting-point, rate of crystallization, source of wax and other variables. It was concluded that the low-melting material contained a large proportion of isoparaffins and the high-melting wax contained largely normal paraffins.

Gruse and Stevens (11) said that waxes isolated from higher-boiling petroleum constituents are microcrystalline. The waxes from distilled residua and cylinder stocks were more microcrystalline and softer. "Petrolatum probably contains the ceresins present in crude oil residua mixed with liquid hydrocarbons of similar molecular weight and high boiling point."

The investigations of Padgett and co-workers (19, 20) dealt with the behavior or crystallization of petroleum waxes and the effects of substances interfering with crystal growth. According to them, paraffin, i. e., paraffin hydrocarbons, wax crystals are orthorhombic (hexagonal rhombic plates). Padgett believed that there are plates, needles, microcrystalline and possibly amorphous forms in petroleum waxes. The isoparaffins were found to make up about twenty percent of petroleum waxes and cyclic paraffins were possibly present. The same compounds might crystallize as either plates or needles, depending on the adsorption of foreign substances at the crystal surfaces.

According to Wilson and Downer (27), waxes may be placed in three categories: 1. fully refined paraffin waxes, 2. scales and partly refined scales, and 3. petroleum ceresins. They list eleven tests which may be applied to the first two. Since Wilson and Downer include practically all of the tests commonly made upon waxes, the tests and some of their conclusions are listed here. They are:

1. Color - no quantitative deduction can be drawn.
2. Odor - a valuable qualitative guide.
3. Taste - can detect presence of traces of light oil.
4. Acidity - is measurable.
5. Moisture - is measurable.
6. Stability to Light - is measurable.
7. Density and Aniline-point - not suitable basis of evaluation.
8. Sweating Test - suitable for some substances.
9. Setting-point - can not determine absolute values since solid solutions exist.

10. Solidification and Plasticity - no simple test.

11. Oil in Wax - no satisfactory test.

For the ceresins, defined as waxes which should have microcrystalline structure and which should give a hard metallic ring, they give no specific tests.

The principal constituents of petroleum waxes are normal, straight-chain hydrocarbons. With increasing molecular weight, branched-chain or isoparaffins, naphthenes, and aromatic compounds are found in increasing amounts. Waxes were until recently classified into two general types, crystalline and amorphous. The former were obtained from wax distillate, the latter from cylinder stock or tank bottoms.

Both types of wax have recently been recognized as actually crystalline, but the crystals of the material formerly classified as amorphous wax are very small, hence, microcrystalline, and probably consist mainly of isoparaffins and behave physically as a colloidal material. Modern theory classifies waxes into the two types, microcrystalline and macrocrystalline, corresponding to amorphous and crystalline, respectively. It still seems probable, however, that some hydrocarbons may exist in waxes in an under-cooled liquid state because these hydrocarbons crystallize with great difficulty. They are found in large proportion in petroleum and they can be isolated as oil from most of the microcrystalline waxes. They may best be referred to as simply "oil". This particular experimental project deals with microcrystalline wax, which has been heretofore little studied.

There are two theories which attempt to differentiate between microcrystalline and macrocrystalline waxes. One is based upon the idea of a plasticizing material; the other is based upon chemical composition. The plasticizing material, the "oil" of the preceding paragraph, is

^t
Thought to bring about the formation of microcrystals rather than macrocrystals by adsorption of this oil at crystal surfaces. It may be the same as or bear a relation to Buchler and Graves' "soft" wax, the lower members of Ferris, Henderson, and Cowles' series of waxes, or Padgett's foreign substances. On the basis of this theory the microcrystalline wax should become macrocrystalline if the plasticizing material were removed. According to the other theory, the chemical composition determines the crystalline state of the wax. Thus, conceivably, ordinary paraffin wax is largely composed of straight-chain hydrocarbons, microcrystalline wax of isoparaffins. There seems some reason to believe that the plasticizing material may be naphthenes or aromatic compounds. As yet, there has been no chemical support for this.

The raw material from which microcrystalline waxes are made is found in tank bottoms. The petroleum in tanks has been allowed to stand for long periods while being subjected to variations in temperature. The components of higher molecular weight have been segregated at the bottoms of the tanks by gravitational separation, as crystals, during cold weather. Tank bottoms also contain water, asphalt, unsaturated hydrocarbons, and dirt.

In preparing microcrystalline waxes, this raw material is first heated to remove water and volatile materials. Sulfuric acid is used to destroy resinous materials. Further purification may be carried out by crystallization from ethylene chloride or other solvents. The solvent is easily removed by distillation. In the preparation of the finer grades of waxes, the molten wax is run through a clay filter bed. This filter is usually composed of an activated clay which is kept at a temperature higher than the melting-point of the wax. The final molten product is run

into tanks for keeping until it is cast in flat slabs for marketing purposes.

Petroleum waxes have been used for very diverse purposes for many years. For example, microcrystalline wax was first used in candles, because paraffin has a tendency to bend when it becomes warm while the former does not. Other properties of waxes such as adhesiveness, setting, value of melting-points, tensile strength, oil content, resistance to acid, alkali, moisture and electricity, and changes in properties with blends of different waxes must be utilized in industry. Microcrystalline waxes are in great demand for industrial use in the manufacture of waxed paper, matches, insulating materials, compounding material in floor waxes and polish, and protective coatings for fresh vegetables. Since the beginning of the war, these waxes have become indispensable in various military applications. The protection of polished machine parts, rationers, clothing, etc., which had to be shipped for great distances and especially to South Pacific areas, was a problem solved by the use of these waxes as a protective coating on paper. In electrical insulating materials, the microcrystalline wax fills the qualifications for a high-melting wax. High melting-point is essential because the electrical properties of waxes tend to change at the melting-point.

It can readily be seen that the industrial world must list microcrystalline wax as one of its highly important products. It is produced to the extent of millions of pounds per month.

PRELIMINARY CONSIDERATIONS

Density and Specific Volume

Density is defined as the mass per unit volume of a substance, commonly expressed as grams per milliliter. Specific volume is the reciprocal of that value, expressed as milliliters per gram. Some reasonably accurate density values have been produced for macrocrystalline waxes, but little work has been done on microcrystalline waxes.

The density of a wax at a single temperature is of little value as compared with a set of density values from low temperatures to temperatures well above the melting-point. The densities of waxes are, in general, so little different among themselves at a given temperature and so dependent upon thermal history and other factors that this property cannot be used in characterizing them or in distinguishing one from another. Study of the relation of density to temperature, however, reveals characteristic and definite properties.

Breaks in the curves found when density is plotted against temperature indicate phase changes, which are of value in identifying substances and in establishing melting-points and transition points. For a satisfactory understanding of the nature of a wax, therefore, the density-temperature relationship over the whole range involving such changes is necessary.

Six methods for determining densities are listed by Reilly and Rae (22). Heiberg (13) gives a seventh. Ward, Kurtz, and Fulweiler (25) have given a fairly complete discussion of densities except that they consider only four methods of determination. These methods are listed below, together with general comments about them.

Volumetric Method

The volumetric method is the simplest form of density determination. It involves measuring the weight and dimensions of solid bodies when these can be prepared in definite geometric form and without inclusions of foreign material.

This is an impossible method to use in our work, for waxes shrink greatly on cooling from melts, forming cavities. They also occlude air (1), even when they are not obviously porous, owing to their crystallinity, so that bodies carved from cakes of wax tend to be heterogeneous. This method cannot serve for molten waxes.

Falling-Drop Method

The falling-drop method of Heiberg (op. cit.) depends on the measurement of the time of fall of a drop of oil in an alcohol-water solution. The specific gravity (in our case, density) is then determined by direct conversion of the time of fall from a calibration curve for the solution. It may be used for molten waxes.

The theory of the method is based upon the fact that when a small body moves through a fluid so slowly that the latter flows past it in smooth stream lines, the relative velocity between the body and the fluid may be obtained from Stokes' Law. The apparatus itself is simple, consisting of a constant-temperature bath, three cylinders containing different proportions, as required by the experiment, of alcohol-water solutions, and a calibrated pipet. The technique involved would require practice.

For viscous oils and waxes, Holberg overcame the difficulty of interfacial tension by rubbing a very small quantity of soap on the tip of the pipet.

He says, "An appreciable error arises in determinations with waxy oils, or with wax, due to the change in volume of wax upon crystallization, but this error may be eliminated by selecting similar waxy oils or waxes as the calibration standards." The upper range in specific gravity was limited by the oils being too dark for the meniscus of the pipet to be discernible. Since 71°C. was about the highest temperature found practicable for operation without excessive evaporation of the ethyl alcohol-water solution, waxes which are too viscous at that temperature could not be handled.

Flotation Method

In this method a solid is immersed in a mixture of mutually soluble liquids, one of which is more, the other less dense than the solid, and the density of the medium is adjusted by adding one or the other liquid until the body remains suspended in the liquid, neither rising nor sinking. The density of the liquid is then determined by means of a hydrometer.

Alcohol and water have been found suitable liquids for use with fats and waxes of plant and animal origin at approximately room temperature. A constant-temperature bath (30°C.) containing a cylinder of the alcohol-water mixture was used. The pellets of wax were at first prepared by rolling them between the fingers, but a much better procedure is to melt the wax on a large stirring rod and allow it to run

down and solidify at the end. A few hours aging puts the wax in a reproducible condition.

It was found that bubbles of air adhere tenaciously to the pellets of wax, but these can be removed by manipulation with a stirring rod. In the experiments conducted at 30°C., all of the waxes available were found to have very nearly the same density in all cases. Other methods indicated that no such sameness existed, so it was concluded that the method is not suitable at this temperature. It would be difficult to apply it over so wide a range of temperature as we desire to cover. Some solvent action on the pellet surfaces can hardly be avoided and it is also difficult to be sure of the homogeneity of the pellets. This method is of doubtful value.

Displacement Method

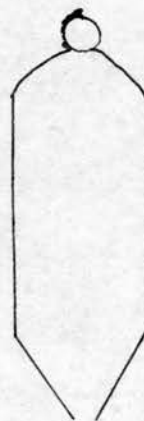
The displacement method is based upon the principle of Archimedes, viz., a body which sinks in a liquid displaces its own volume of the liquid. The procedure involves weighing the object, wax, first in air, then when suspended by means of a wire in a liquid of known density. The loss in weight of the wax divided by its volume gives the density.

This method is subject to several difficulties. Failure in wetting the solid or in removing air bubbles is a great potential source of error. Also the effect of surface tension of the liquid upon the suspending wire causes inaccuracies in weighings.

The displacement method should be applicable to all solid waxes over a range of temperatures up to the melting-point. The values should be accurate if one can be sure that the wax does not contain gaseous or other inclusions.

An apparatus of great interest based upon this same principle is the Young-Eimer and Amend gravitometer illustrated in the Fisher apparatus catalogue. It employs a compound pendulum with an arm and needle for holding the sample and another arm which moves over a scale. The object is fastened on the needle and a weight acting as counter-balance is adjusted to bring the indicator to a definite point on the scale. An electrical vibrator acts to eliminate sticking of the bearings. A beaker of water is then brought up from below and supported so that the object is immersed. The density of the body is then read directly. The limits of specific gravity which may be determined are given as 0.90 to 10.00 grams per milliliter, but it would probably be possible to extend this range.

A method for determining the densities of animal fats over a range of temperatures has been described by Williams (26). It gives a very clean-cut density curve with lard and other such fats with breaks at both the upper and the lower limits of fusion. It would presumably serve equally well for waxes in the molten or the solid state. Potentially it seems the most promising of the density methods for our purpose. It employs a glass bell of the form shown at the right. The constricted mouth permits this bell to be transferred from vessel to vessel when filled with water without admitting bubbles of air. It is first weighed, filled with water and then immersed in water in a suitable vessel. The wax to be studied is

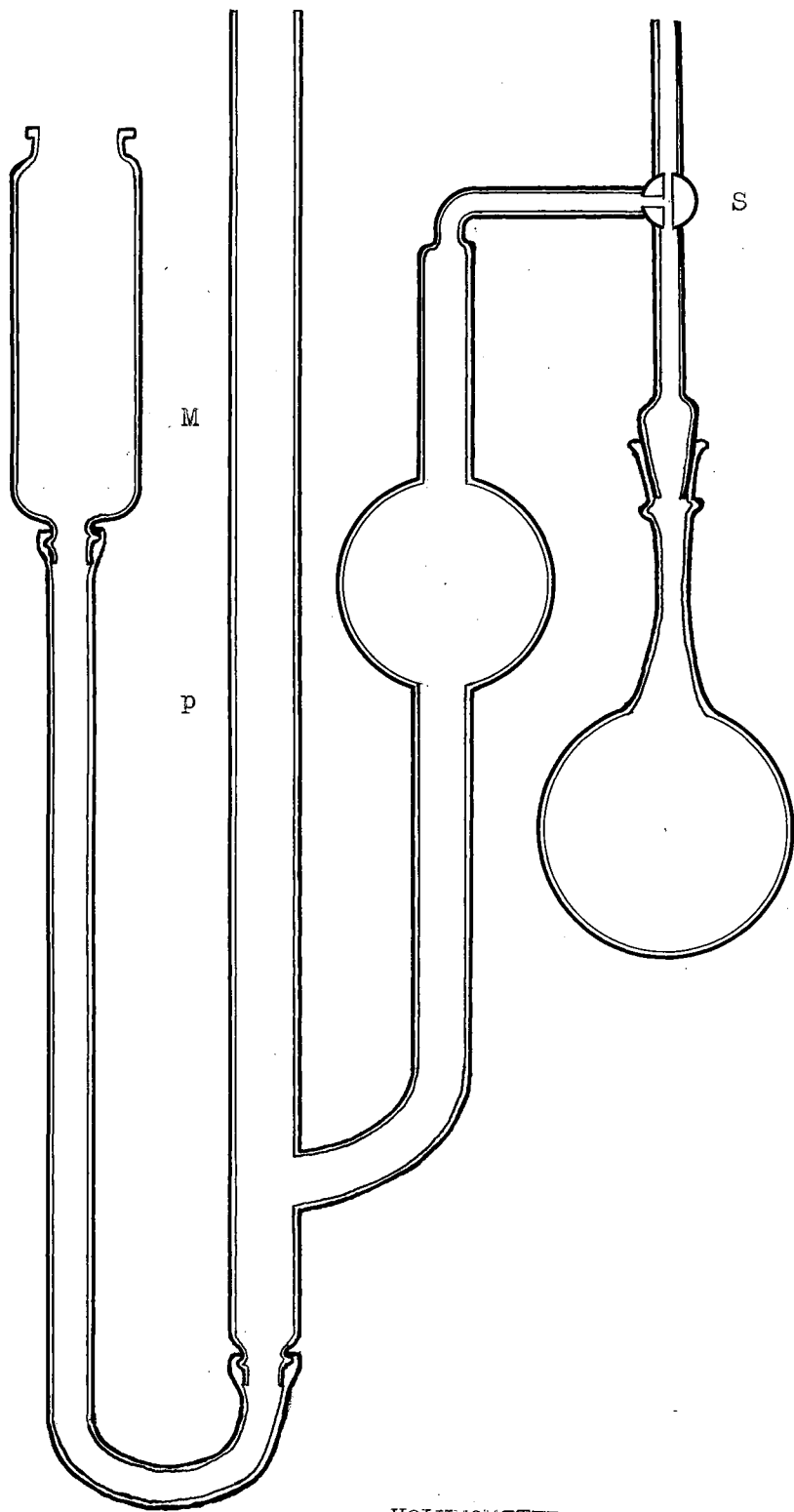


melted and freed of dissolved air. The water with its immersed bell is heated above the melting-point of the wax. The wax is then sucked up in a heated pipette with recurved tip and delivered upward into the bell. If w is the weight of the fat, w' , the weight of the bell and fat in water, and d , the density of water all at temperature t , the density of the fat is given by the expression $D_w = \frac{wd}{w + s + w'}$.

Experiments with this device have been tried with microcrystalline waxes. It is very difficult to eliminate air from these waxes to such an extent as to exclude bubbles. Even when they have apparently been eliminated at the temperature of filling they will often appear on heating or on standing for some time. Williams allowed the filled bells to stand at room temperature for twenty-four hours or longer before beginning the experiments. The problem of maintaining the water above 60° and up to 100°C . while the measurements are being made is a considerable one. The temperatures covered by Williams in his work ranged from 15° to 50°C . It is possible that ethylene glycol or some similar liquid might be used but the hygroscopicity of this solvent would be a difficulty. So far as our experiments have gone, no way out of the difficulties which this method presents have been found.

Volumometer Method

Several modifications of the volumometer have been used in density determinations. The only one which seems applicable to this material was designed and used by Regnault. Mercury is conveniently employed as the working liquid. The apparatus is shown in Figure 1. It may be employed in two ways.



VOLUMOMETER

Fig. 1.

1. Set the leveling bulb so that mercury in the side tube and the volumometer tube stand at the height p with stopcock S open to the vessels and the air. Then close it so as to connect the two sides of the apparatus, but cut it off from the air. Now raise the leveling bulb so that the mercury level in the volumometer tube is brought to M and measure the difference in height, h . Let the prevailing barometric pressure be P , the volume between p and M be v , and the volume of the space above M and including the bulb be V . We have: $P(V - v) = (P - h)v$, whence $V = Pv/h$. Now introduce the unknown solid and repeat. A new volume V' will be found. $V' = V - v'$ where v' is the volume of the solid which has been introduced. v' , then, $= V - V'$.

A difficulty which may well be found in the method of this form is the possibility of leakage of the ground-glass stopcock.

2. Alternatively, one may set the leveling bulb so that the level of the mercury in both tubes is M with the stopcock open. Then, closing it as before, the leveling bulb is dropped to bring the mercury level to p , and the height h' is found. Now we have $PV = (P - h')(V - v)$ and $V = v(P - h') / h'$. The solid is introduced and the experiment is repeated to find the new volume. $V' = V - v'$, whence v' is found as before by subtraction. The density can then be calculated.

The volumometer method has three important limitations:

1. The temperature throughout must be constant during the measurements.
2. The apparatus and the sample must be free from water or other volatile substance.
3. The solid must not be capable of adsorbing gases.

When one immerses the bulb with its wax in a bath at somewhat elevated temperature, as will be done in making the measurements which are desired, uncertain and difficultly reproducible conditions are introduced. Further, it is difficult to make sure that all water and other volatile substance has been removed from the apparatus. Micro-crystalline waxes, which tend to be porous, adsorb gases. All waxes yield gas on melting. Some of these difficulties can be avoided by employing both of the procedures which have been described and taking the average of values if they are not too divergent. In general, however, this method does not seem promising for our purpose.

It is claimed that the accuracy of the method may be as great as 0.1 per cent under the best conditions. The best that we have been able to get at room temperature is an accuracy of 1.0 per cent. No experiments at elevated temperatures have been tried.

Pycnometer Method

Pycnometers are available in many different forms. In principle the pycnometer must hold a definite and accurately reproducible volume of liquid at any desired temperature. Three types of pycnometers are useful in work with waxes. The bottle type with small, ground-in, capillary stopper is satisfactory, except that it is difficult to clean, fill, or empty. The type employed for densities of pitch has as a stopper nearly as large in diameter as the vessel itself with a capillary hole through it. This pycnometer is much more convenient, but less accurate than the former one. The conical type has a large mouth with a ground plane top so that a definite volume of liquid can be enclosed by sliding a plate over the mouth after the vessel has been filled. This

type is convenient and capable of great accuracy.

The volume of the pycnometer is found by determining the weight of water, or other standard liquid which it holds, and dividing by the density of the liquid. The system must be held at a definite temperature. The density of a solid, such as a piece of wax, is determined by introducing a sample (less than five grams) into a pycnometer of approximately twenty-five milliliter capacity. Before the liquid is introduced, the pycnometer is heated in an oven above the melting-point of the wax. Then the pycnometer with its molten wax is rotated slowly so that the wax adheres as it cools along the sides and bottom of the vessel. This helps to eliminate bubbles of air which would otherwise be enclosed in the wax. As soon as the wax appears solid, warm distilled water which contains a small amount (0.01%) of saponin and has been boiled to remove air is introduced into the pycnometer. The system is brought to constant temperature, and the pycnometer is closed and weighed. Corrections are made for the density of water at that temperature. The volume of the pycnometer (previously calculated), the weight of the wax, and the volume of wax (from difference) are known. The density of the wax is found at a particular temperature by dividing the weight of the wax by the volume it occupies.

The method is not so easy as it might seem; moreover, there are several sources of error. Even with the precautions taken as given above, the fact that the wax pulls away from the sides of the glass giving spaces which often cannot be filled with liquid presents difficulties. It is also impossible to do away with the tendency of air to dissolve in the wax (1). The nature of the wax itself is important in considering the accuracy of this method. Certain waxes are relatively highly porous and tend to include more air than do other waxes. They

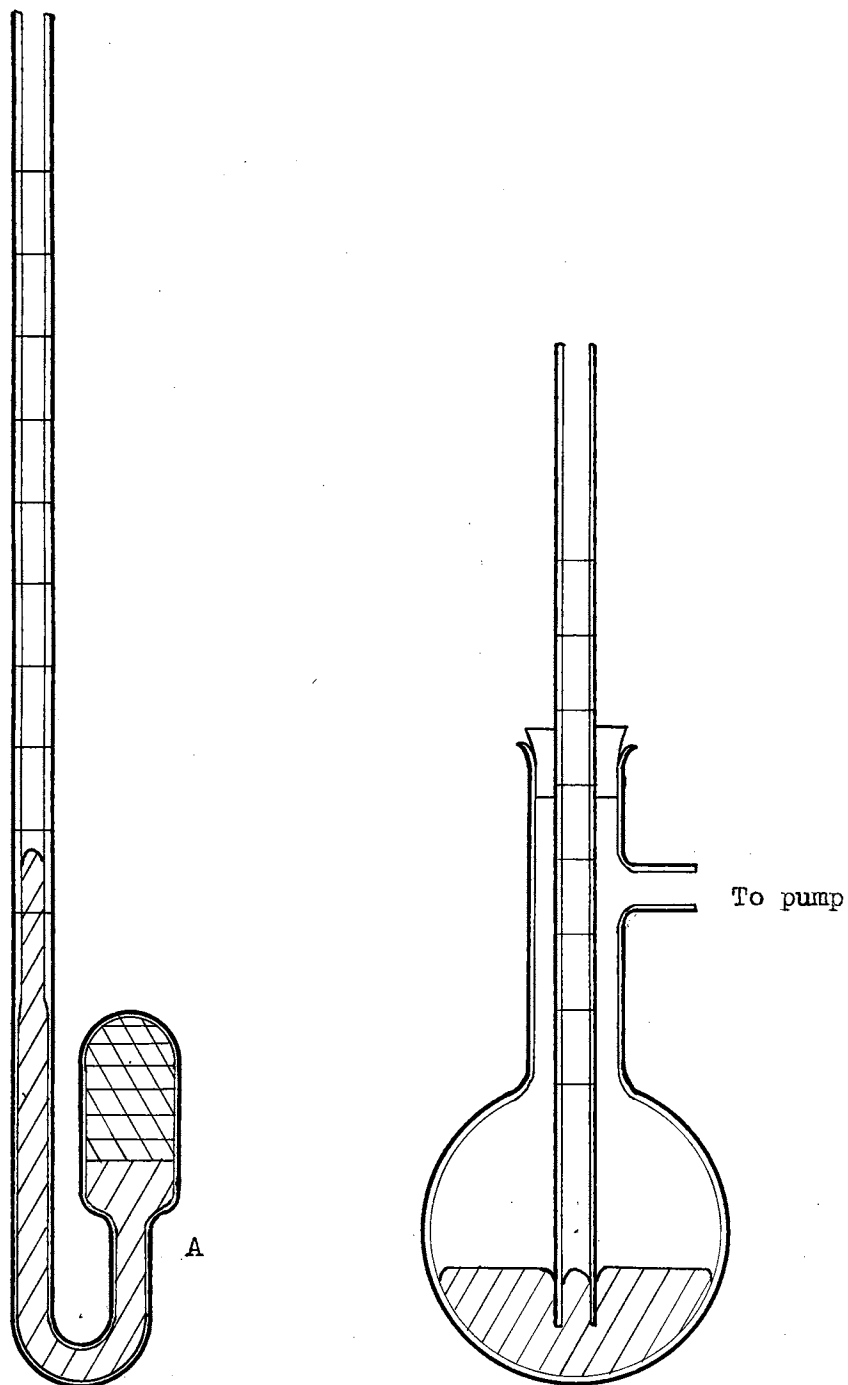
also tend to pull away from the walls of the vessel to a greater extent.

When working with molten waxes, one usually finds density values of the order of 0.75 grams per milliliter. There is no suitable liquid having a density less than that to be expected for the molten wax at the temperatures which must be reached. The liquid to be used in the experiment must not float the wax out of the pycnometer. Experiments, therefore, cannot be carried through from the solid to the liquid state without change of specimen. The pycnometer may, of course, be filled completely with molten wax. This will make the determination of densities over the complete temperature range yet slower; they are very time-consuming at best. By using the pycnometer method, we found density values at lower temperatures which checked with values secured by other methods. The method is increasingly inaccurate at elevated temperatures. The Institute of Petroleum (24) gives the pycnometer method as one of the standard methods for density determinations.

Dilatometer Method

The dilatometer is defined by Wood and Brusie (28) as a vessel with upturned capillary exit for measuring volumes of a liquid by the amount of mercury expelled at various temperature. The form used in this work is shown in Figure 2. In this dilatometer the wax is confined above a column of mercury. The mercury extends over to the scale, upon which volumes characteristic of the conditions are read.

In preparation for an experiment a tared bulb of the form shown in the figure was prepared and a sample of wax was introduced, melted, allowed to cool, and weighed. The remaining portion of the dilatometer was then sealed on. Mercury was put into a shortnecked distilling flask



DILATOMETER AND METHOD OF FILLING

Fig. 2.

and the stem of the inverted dilatometer was introduced through a rubber stopper as shown. The flask was rocked back to expose the open end of the dilatometer and the whole was pumped out to remove air, using a Cenco Megavac oil pump. Tilting it again and releasing the vacuum slowly permitted mercury to enter and fill the dilatometer. Further pumping resulted in the release of more gas, the evolution of which could be detected by its bubbling through the mercury. When no more gas could be extracted the dilatometer was righted and set in boiling water to melt the wax. Any gas not already removed was at once apparent as bubbles in the wax. Pumping was repeated if necessary until no gas bubbles were present in the melted wax. The level of mercury in the bulb was adjusted near the highest mark when the bulb was held at the highest temperature to be used in the following experiment or near the zero mark at low (room) temperatures. For the measurements the dilatometer was immersed to the zero mark in a constant-temperature bath using gas oil or water as liquid and volumes were read off at observed temperatures. From thirty minutes to several hours were allowed for equilibrium to be reached in the system, the final test for this condition being the constancy of the reading over a period of fifteen to thirty minutes. After the readings were complete the whole assembly was weighed. This gave the weight of dilatometer plus wax plus mercury. The mercury was next removed. The wax^x was dissolved and removed completely by washing out with benzene with the aid of a suction flask. The cleaned and dried dilatometer was then weighed empty. Finally the dilatometer was filled with boiled distilled water to a point on the lower part of the scale. It was brought to a known temperature in a constant-temperature bath for exact determination of the level reached

and then weighed with the water. The volume of the dilatometer to the zero mark was found. The total volume occupied at each of the experimental temperatures, the volume occupied by the mercury, and the volume of the wax were calculated. This volume divided by the weight of the wax gave the specific volume at each temperature, and the reciprocal of each of these specific volumes gave the respective density.

This procedure is very time-consuming. An obvious improvement would be brought about if a ground-glass connection could be introduced at A and kept tight by pulling the two members of the apparatus together by means of springs. Several modifications of this arrangement have been tried with mercury, ethylene glycol and water as dilatometric liquids, but without success. These joints always leaked at elevated temperatures.

Densities have been determined for seventeen waxes and blends of waxes using the technique outlined above.

It was found more suitable to use the dilatometric readings found on slow cooling rather than those found on slow heating. The earlier runs employed the heating method, but since it is more time-consuming, the later determinations were made by the cooling procedure.

It is necessary to allow sufficient time, sometimes several hours, for the system to come to equilibrium. Even then it is sometimes hard to duplicate results. For example, when the system has been allowed to stand at room temperature overnight, the following day's readings must be brought to the final reading of the previous day, in order to check previous readings. The fact that this may yield different results indicates that the density of microcrystalline wax is determined by its thermal history. To eliminate this possibility, it is necessary to keep the process in continuous operation until all determinations

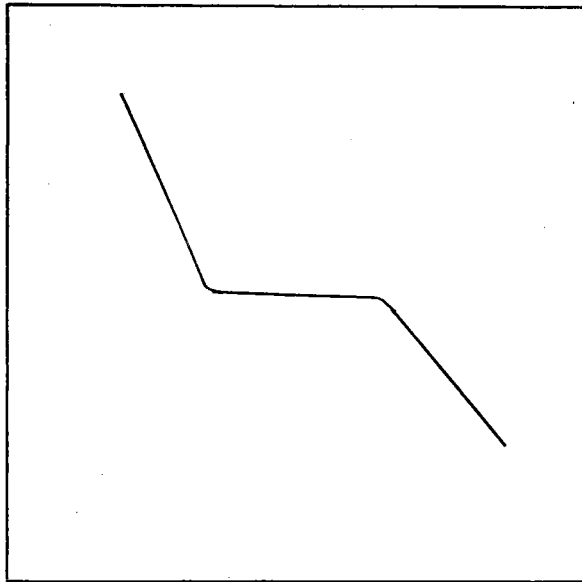
throughout the complete range of temperatures are made. It is much more difficult to duplicate the lower temperature readings because the wax tends to pull away from the walls leaving vacuum voids. Since these values are usually below any wax freezing-point, the effects on the succeeding calculations are relatively unimportant. The color characteristic of the wax in bulk was found only after the wax had stood at constant temperature. It seems that aging for two or three hours is sufficient to bring the wax into a reproducible state. Some workers have found it necessary to maintain waxes at room temperature for twelve hours or more in order to get satisfactory results.

Cooling Curves

Cooling curves are found by plotting the consecutive temperatures of a cooling mass read at short intervals of time. With pure substances, starting with the molten material, the curve secured by plotting temperature against time falls rapidly at first. When crystals begin to separate, the curve shows a plateau, the temperature remaining constant until all of the sample has frozen. The horizontal portion of the curve serves to define the freezing-point of the substance. The freezing-point is that temperature at which solid and liquid are in equilibrium; the initial freezing-point is that temperature when melting is complete. The curve will be of the form shown in Figure 3.

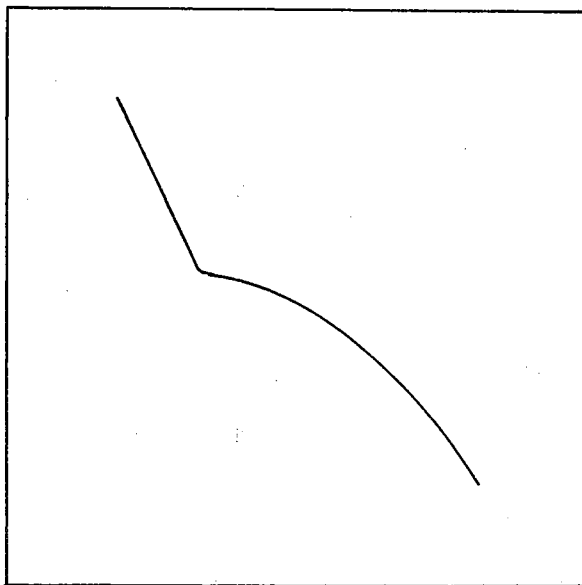
When the melt is impure or in case the solid in freezing forms mixed crystals or a solid solution, the curve takes the form shown in Figure 4. The first halt in the cooling curve is the initial freezing-point. Beyond this point the temperature falls off more and more rapidly as time passes until the whole mass has solidified. Then it cools in the same manner as does any solid. The form of the cooling curve which is found serves to differentiate between pure substances and mixtures and may give some indication of the nature of the solid which is separating.

The A.S.T.M. (3) method is one type of melting-point determination that can be employed. In it the wax sample is placed in a test tube and heated in a water bath to a temperature not higher than 15°C . above the melting point. A thermometer and stirrer fit into this tube through a tight stopper. This setup is fitted into a large tube which, in turn, is placed within a constant-temperature bath.



Typical Cooling Curve for a Pure Compound

Fig. 3.



Typical Cooling Curve for an Impure Compound

Fig. 4.

At the beginning of the experiment, the temperature of the water bath should be approximately 10°C . below the melting-point of the wax. The test tube containing wax is placed in the air bath. The wax is stirred continuously during the rest of the experiment while the temperature is read every fifteen seconds. The melting-point is taken as the average value of the first five readings that lie within a range of 0.1°C .

The I.P.T. method for melting-point determination is essentially the same as the A.S.T.M. method with the exception that the wax is not stirred.

EXPERIMENTAL WORK

In the following experiments eleven waxes were used singly and in blends in the determinations. Wax C is a so-called mealy microcrystalline wax. It is hard and brittle. The term "mealy" refers to the fact that it can be readily broken up into a powder, like meal, owing to the nature of its fracture. Wax B1, Wax B3, Wax B2, and Wax Q are microcrystalline waxes referred to as "plastic" owing to the fact that they break down to threads or filaments rather than to powder under abrasion. (The numbers give, roughly, the respective melting-points of the waxes in degrees Fahrenheit.) Wax B3R and Wax CR are residues of the respective waxes, Wax B3 and Wax C, from which most or all of the oily material has been removed by recrystallization. Three wax fractions, 3-150°, 7-110°, and 11-70°, were prepared by careful recrystallization of Wax B3. The samples were prepared specifically for x-ray examination by the project sponsor. The first number is the number of the fraction, the second, the temperature of separation in degrees Fahrenheit. The paraffin Wax, a household product manufactured by one of the major oil companies, has an initial freezing-point of 54.8°C.

<u>Specimen</u>	<u>Approx. Melt. Pt.</u> <u>(ASTM D-127)</u>	<u>Color</u>
Wax Q	150°F	Yellow
Wax C	190/195	Yellow
Wax B1	170/175	Yellow
Wax B2	170/175	White
Wax B3	190/195	Yellow
Sonneborn Petrolatum	120° F	White
Paraffin Wax	128	White
3-150	197	White
7-110	163	White
11-70	171	White

Densities of Waxes

Densities of waxes were determined by the dilatometric method from about room temperature to well past the melting-point of each substance. The method has been described above. The method of calculation is illustrated in detail by the following calculation for Paraffin Wax:

A. Weight of bulb	8.4459 gm.
B. Weight of bulb + wax	11.9968 gm.
C. Weight of dilatometer + mercury + wax	90.2995 gm.
D. Weight of dilatometer	31.4805 gm.
E. Weight of dilatometer + water, 20 C., read. .118 ml.	39.3315 gm.
a. Weight of wax (A - B)	3.5509 gm.
b. Weight of mercury (C - (D + a))	55.2681 gm.
c. Weight of water (E - D)	7.8510 gm.
d. Volume of water, 20°C., read. .118 ml. (c x 1.0018)	7.8651 ml.
e. Volume of water, 20°C., read. .000 ml. (d - .118)	7.7474 ml.
f. Total volume (Volume read + e)	(see chart below)
g. Volume of mercury (b x d. of mercury, respective temp.)	
h. Volume of wax (f - g)	
i. Specific volume (h / a)	
j. Density (1 / i)	

Temperature °C.	Volume Read	Total Volume	Volume of Mercury	Volume of Wax	Specific Volume	Density
0	.182	7.9294	4.0650	3.8644	1.0882	.919
5	.192	7.9394	4.0689	3.8705	1.0900	.917
10	.210	7.9574	4.0726	3.8848	1.0940	.914
15	.228	7.9754	4.0763	3.8991	1.0981	.911
20	.242	7.9894	4.0800	3.9094	1.1010	.908
25	.262	8.0094	4.0837	3.9257	1.1056	.904
30	.300	8.0474	4.0874	3.9600	1.1152	.897
35	.350	8.0974	4.0911	4.0063	1.1282	.886
40	.400	8.1474	4.0948	4.0526	1.1413	.876
45	.455	8.2024	4.0985	4.1039	1.1557	.865
50	.580	8.3274	4.1022	4.2252	1.1699	.840
55	.650	8.5974	4.1059	4.4915	1.2649	.791
60	.909	8.6564	4.1097	4.5467	1.2804	.781
65	.930	8.6774	4.1134	4.5640	1.2853	.778
70	.950	8.6974	4.1171	4.5803	1.2899	.775

Density Curves
Paraffin-XXXX Series

% XXXX	Wax C
1.	0.0
2.	10.3
3.	30.4
4.	50.3
5.	70.0
6.	89.5
7.	100.0

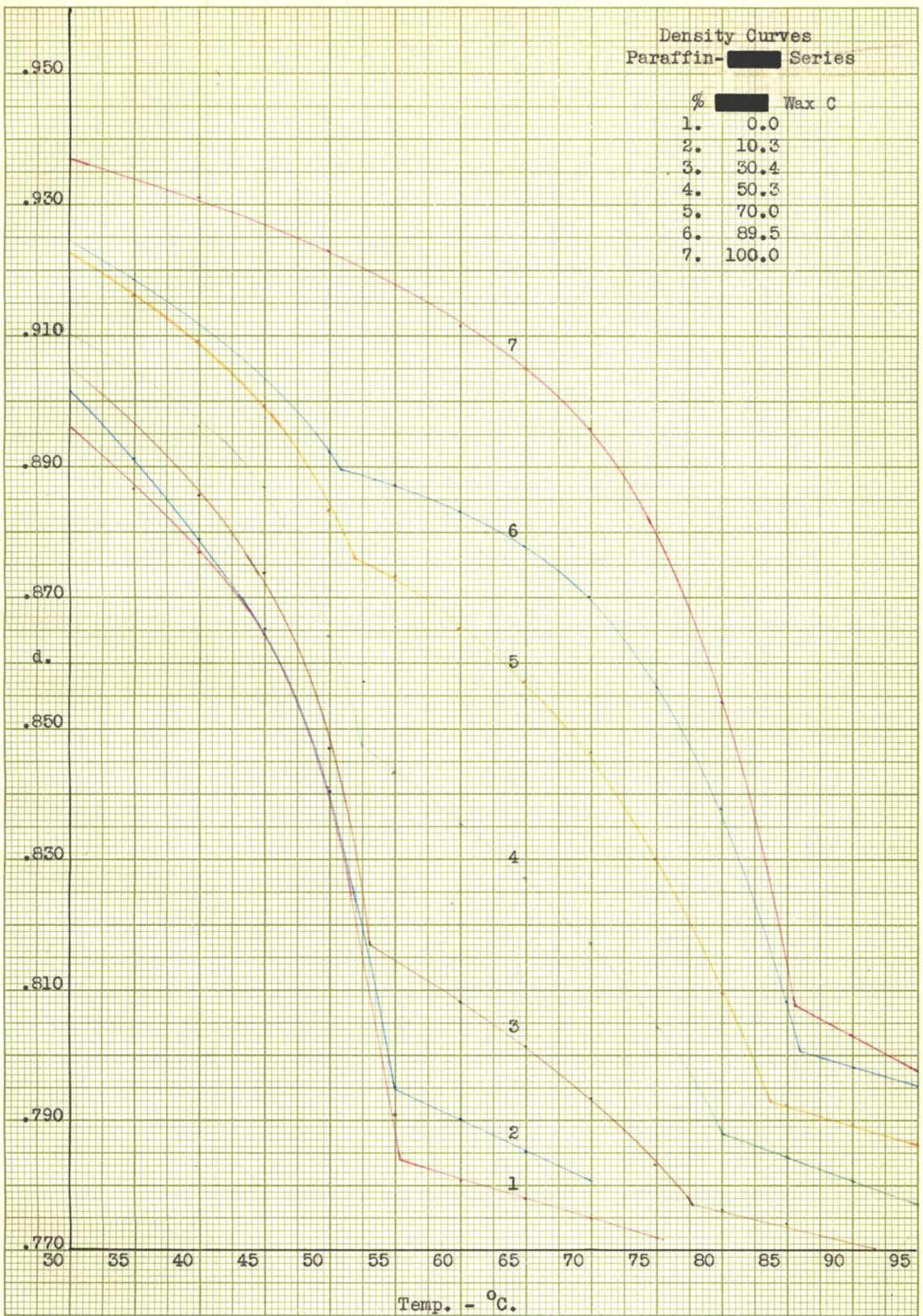


Fig. 5.

Density Curves
 Paraffin-XXXXXXXXXX Series
 % XXXXXXXXXX Wax B3

1.	0.0
2.	36.2
3.	51.9
4.	67.4
5.	100.0

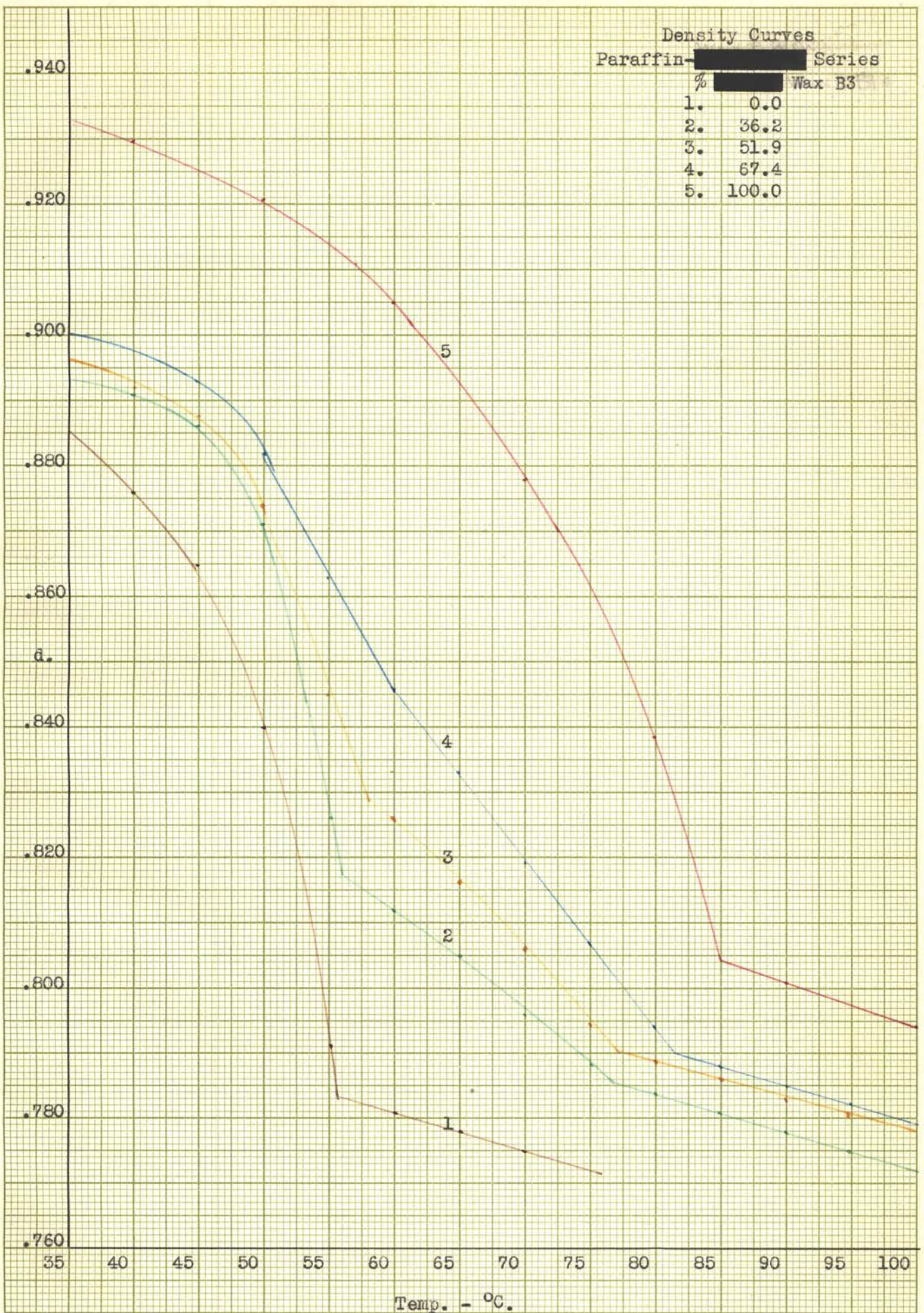


Fig. 6.

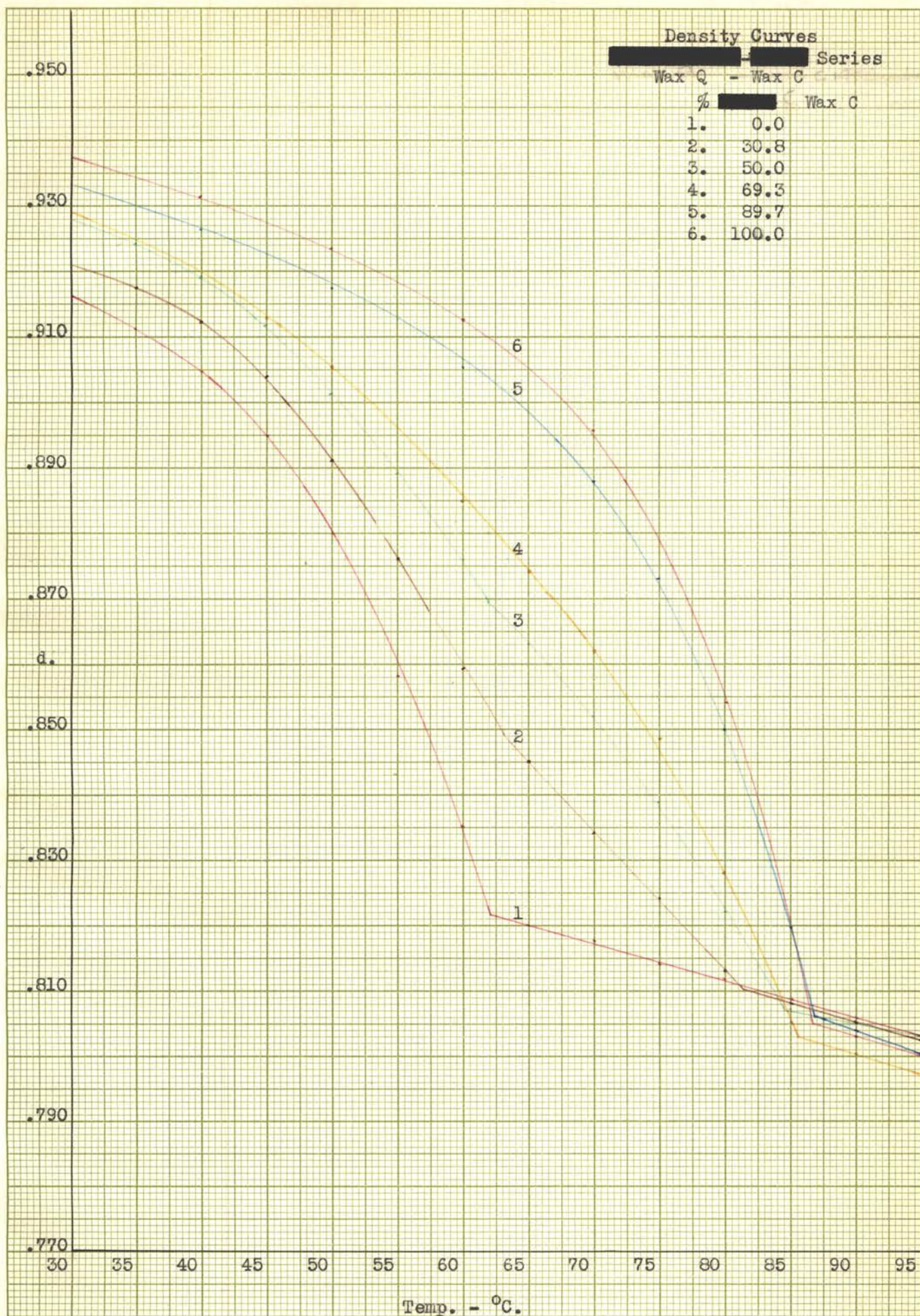


Fig. 7.

The data for all of the waxes and blends of waxes are represented graphically in Figures 5, 6, and 7. The results found on plotting these density-temperature curves are of interest.

The curves of single waxes which we have run gave one sharp break at the freezing-point of the wax. When the forms of the different curves are compared, they are found to be very similar, particularly when comparing Wax B3 with Wax C.

These freezing-points we have found are actually initial freezing-points. The waxes with which we work contain an unknown number of components, some of higher, others of lower true melting-point. On cooling a molten wax we have observed that an opalescence first appears and persists at a temperature which corresponds, within the limits of experimental error, with the initial freezing-point found in these experiments. This must be a precipitate of the highest melting component present in the wax. On cooling further the precipitate increases in quantity. Perhaps other components separate with the original ones. This continues until the whole of the mass is solid. In fact, composite waxes such as these have no true freezing-point but rather a freezing range of unknown extent. Initial freezing-points (final melting-points) are the only halt-points that are found in the curves representing thermal properties of these waxes as functions of temperature.

Two breaks are found in the curves for all of the blends of Paraffin and Wax C except in Curve 2 (Figure 5), and it would undoubtedly have shown a second break, except that the experiment with this specimen was performed before the occurrence of a second break was suspected, and it was not carried to a sufficiently high temperature to reveal it. In the blends of Paraffin Wax with Wax B3,

Curve 4 (Figure 6) is the only one which does not show a definite second break. However, there is the suggestion of such a break. Similarly, as seen in Curve 5 of the Wax Q-Wax C Series (Figure 7), the high-percentage mixture of Wax C with the other wax did not effect a second break, though the lower percentages do. The correlation of these data with those of cooling curves and of enthalpies will be given later.

Crystallinity Indices

The contraction of petroleum waxes on cooling from the molten state is a familiar phenomenon. In fact, this contraction commonly gives rise to voids in the waxes and makes the determination of their densities difficult or impossible. It is readily seen, too, that the degree of contraction on cooling is different for different waxes. Kinsel and Phillips (14) have made this contraction the basis for a method for classifying petroleum waxes.

Kinsel and Phillips believe that the whole of the temperature range covering the change in volume due to crystallization and that due to crystal-structure change lies between a temperature ten degrees Fahrenheit above the A.S.T.M. melting-point and another fifty degrees below that point. Taking the percentage change in volume between these temperatures for any wax, they use it to define a property which they call the "Crystallinity Index". This is defined by the equation: $C.I. = 10(K_c - 2.4)$ where K_c is the percentage contraction.

Following is the method used in finding the percentage contraction.

"Pour exactly 100 ml. of the wax (whose melting point has been determined according to A.S.T.M. designation D127) heated to 100°F. above its melting point into a 100 ml. mixing cylinder which has been heated to the same temperature. Allow it to cool for two hours protected from drafts and then for two hours in a water bath kept at 50°F. below the melting point of the wax. As the wax cools it will form a cavity running down the center of the cylinder, often covered by a thin layer of wax. Pierce the wax layer at the center with a sharp instrument, such as a pointed glass rod, so that a hole about 2 to 3 mm. in diameter is formed. Add (from a burette) a 50% aqueous solution of glycerol to the 100 ml. mark. Apply a slight vacuum to liberate any trapped air and refill to the 100 ml. mark. The amount of liquid added is the total percent contraction."

Using the crystallinity indices which they found, the authors classified petroleum waxes in three categories. True microcrystalline waxes were found to have crystallinity indices of 65 to 85; semi-crystalline waxes fell in the range 85 to 106; macrocrystalline waxes fell in the range 106 to 117 or (presumably) higher.

We have found that actual density curves could be utilized in determining crystallinity indices just as well as the values found by the method described. Some such curves are available from the literature, and we have been able to add others from our own work.

From our density curves, we found Wax C to have a crystallinity index of 93. In using the Kinsel-Phillips method, a value of 97 was obtained. Wax B3 gave crystallinity indices of 89. Wax B2 gave a crystallinity index of 76. Wax Q gave a value of 71. This puts two of these waxes, Wax C and Wax B3 definitely in the semicrystalline class, but from all other properties we have recognized that all of these waxes should be microcrystalline. Our Paraffin Wax gave a crystallinity index of 106, which places it in the expected macrocrystalline category.

H. Bennett (1) gives density curves for three microcrystalline waxes. For these we find 94 for Cerese A.A. whose melting-point is 170°F. , 74 for Petrosene B, whose melting-point is 166°F. and 55 for Product 2305, whose melting-point is 155°F. (In calculating these crystallinity indices the melting-points of these waxes as given by Bennett were used. He does not give the method by which they were determined.) Of course, melting-point cannot be taken as indicative of degree of paraffinicity or the reverse, but the crystallinity index does not have the relation to melting-point which one would expect. The last two waxes are definitely microcrystalline according to the criteria of Kinsel and Phillips, while the first is semicrystalline.

Of the waxes whose densities are given in Science of Petroleum (25), only one, refined field wax with a melting-point of 194°F. , is to be classed as semicrystalline with a crystallinity index of 94. All of the other waxes whose densities are given there show crystallinity indices that fall in the macrocrystalline category. This is as would be expected from their melting-points and the fact that they are certainly paraffin waxes. The same is true of other waxes for which values are given by Carpenter (4).

Even with the results presented here, more work should be done with crystallinity indices before they can be taken as a sure basis for classifying waxes.

Cooling Curves

From his work in determining enthalpies of some waxes and blends of waxes, Dr. Trimble came to these conclusions: The addition of an impurity, the impurity in this case being a second wax, lowers the freezing-point of the initial wax. The blends of certain waxes showed two breaks in their enthalpy-temperature curves. In Paraffin-Wax C mixtures, the Paraffin lowers the initial freezing-point of Wax C and Wax C lowers the initial freezing-point of Paraffin. To explain the phenomenon of two breaks it must be assumed that the breaks represent, respectively the temperatures at which the high-melting components of one wax end and the high-melting components of the other wax begin to separate from the molten mass. This may possibly mean that the molecules of one wax do not build into the unit cells which are formed by the other wax, but rather remain separate and form unit cells of their own. On the other hand, it may be that, on cooling, the whole of Wax C is solidified before the freezing-point of the highest melting component of Paraffin is reached, so that a second break is found when it begins to separate. If such blends of waxes as this do not form solid solutions they are not homogeneous. This might have important implications for the users of blended waxes. There is, however, no evidence of such a state when the wax is examined superficially. The blends do not show any tendency to separate into two layers whether they are cooled rapidly or slowly. Dr. Nickolls believes that he has found some evidence of such heterogeneity when thin preparations of the blends are formed on microscope slides and

examined under the microscope. Waxes present so many aspects, however, that it is difficult to be sure of this.

Another feature found in the enthalpy curves by Dr. Trimble was the fact that the transition-point (the temperature at which the crystal structure changes from one form to another) of paraffin persists in each curve even though the effect becomes less pronounced the smaller the percentage of paraffin in the blend. This would seem definitely to establish the fact that Wax C and Paraffin Wax crystallize separately when the blends are cooled. The enthalpies of the solid blends are higher than those calculated by the method of mixtures, indicating that some bond which requires energy to break it exists between their component portions.

Preliminary work showed that these phenomena could be detected also by means of cooling curves. This led us to further work with such curves.

The A.S.T.M. melting-point method which was described earlier was not suitable for these cooling curves for it did not show very sharp breaks. We used a small well-evacuated, unsilvered Dewar flask with an internal diameter of approximately one and one-half centimeters. Five grams of wax served to cover the bulb of the thermometer. The thermometer could be read by estimation to a hundredth of a degree Centigrade. The wax was heated to about 10°C . above the melting-point by setting the flask containing it into a beaker of boiling water. The thermometer was then inserted, being held in position by a well-fitting stopper in the top of the flask. The flask was placed in the jacket of a Beckmann freezing-

point apparatus which served as an air jacket. The wax was allowed to cool without stirring, and the temperature was read at intervals of thirty seconds.

As shown in Figure 8, the cooling curves for blends of Paraffin and Wax C show two breaks. Paraffin Wax blended with Wax B3 (Figure 9) gives curves which show two breaks, as do the blends of Paraffin with Wax B2 (Figure 10). Paraffin when blended with Wax CR (Figure 11) and Wax B3R (Figure 12) gives curves which show two breaks, all of which are especially sharp. Wax Q when blended with Wax C (Figure 13) gives a curve with two breaks. However when Wax Q is blended with Wax B2 (Figure 14), there is only one break in the curve. Wax B2 and Wax B1 when blended with Wax C (Figures 15 and 16) give cooling curves that show but one break. Figure 17 shows the effect of Sonneborn Petrolatum in lowering the initial freezing-points of Wax B3 and Wax C. Figure 18 shows the effect of mineral oil in lowering the initial freezing-points of the same waxes. Mineral oil is somewhat more effective than is petrolatum.

Figure 19 is of special interest. It shows the cooling curves of three wax fractions separated from the same original wax, and the cooling curves for their blends. The three simple fractions, Curves 1, 3, and 7, show but one break each. The two fractions separated at the lower temperatures and blended in equal proportions also show but one break (Curve 2). Both of these fractions when blended in equal proportions with the fraction separated at the

Cooling Curves
Paraffin-████████ Series

	% Wax C	Upper Breaks- ^o C.	Lower
1.	0.0	----	54.8
2.	10.3	74.4	54.4
3.	30.4	78.2	53.6
4.	50.0	81.6	53.5
5.	70.0	84.0	52.2
6.	89.5	85.2	50.0
7.	100.0	87.0	----

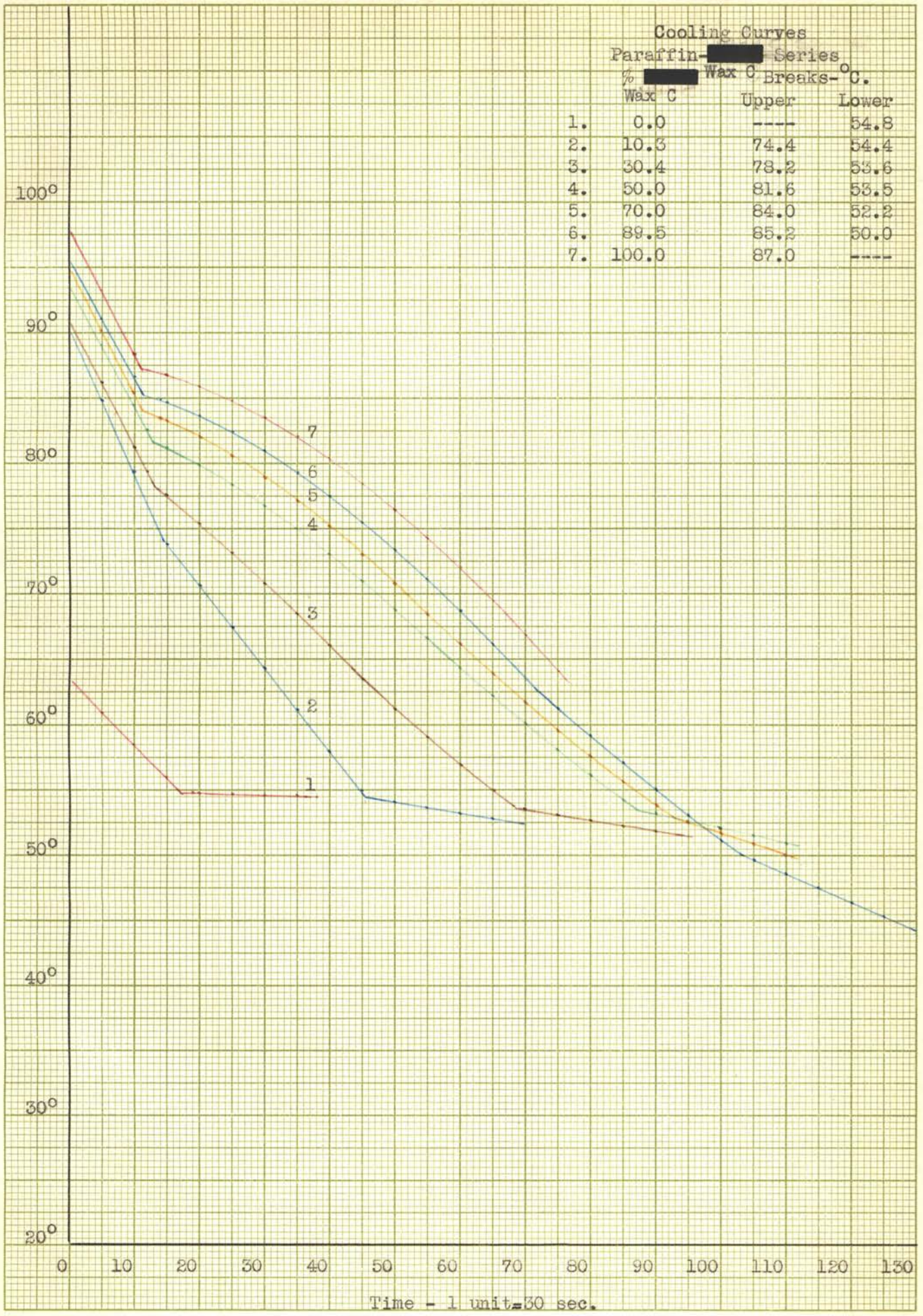
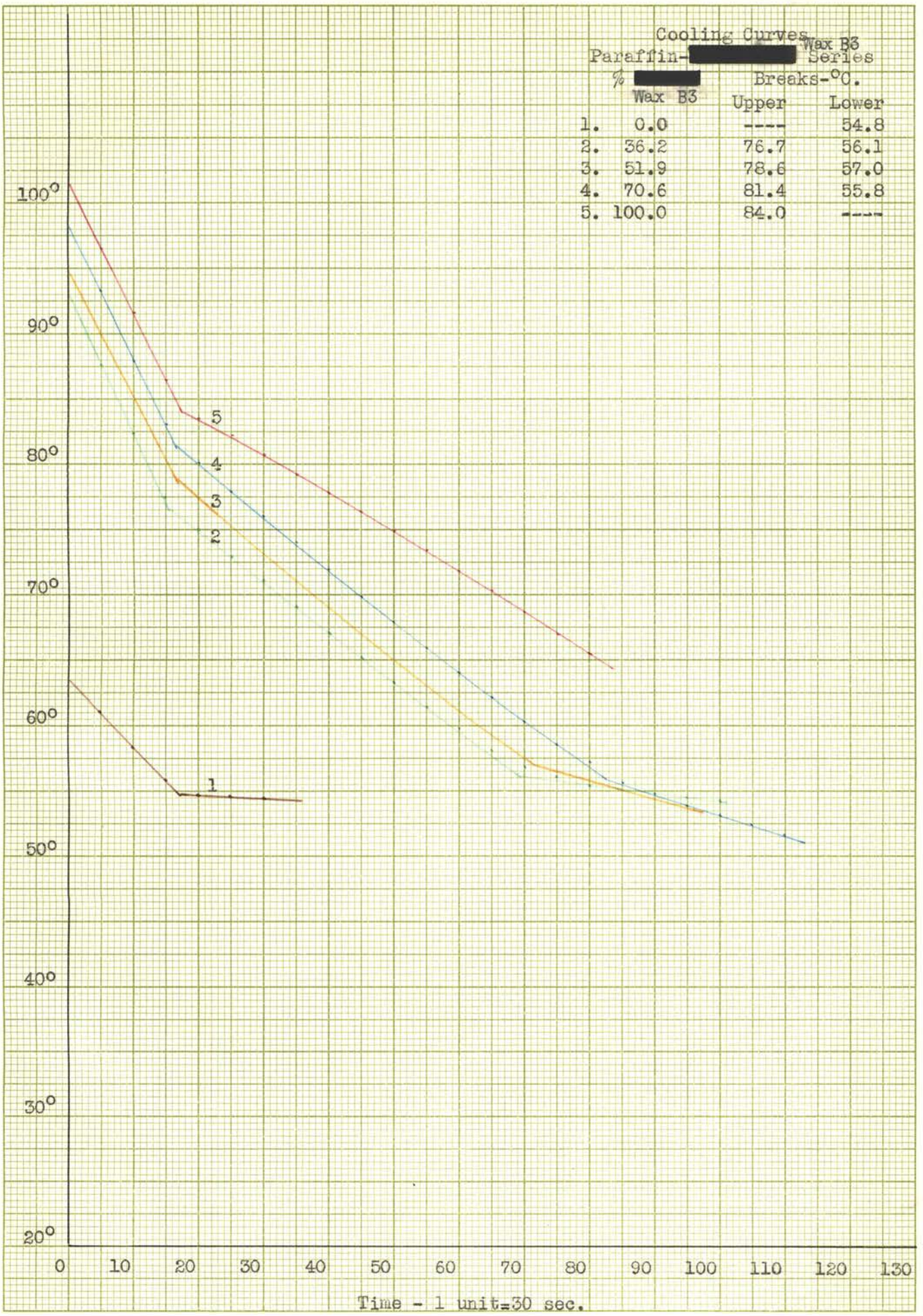


Fig. 8.

Cooling Curves, Wax B3
Paraffin-XXXXXXXXXX Series

	% Wax B3	Breaks-°C.	
		Upper	Lower
1.	0.0	----	54.8
2.	36.2	76.7	56.1
3.	51.9	78.6	57.0
4.	70.6	81.4	55.8
5.	100.0	84.0	----

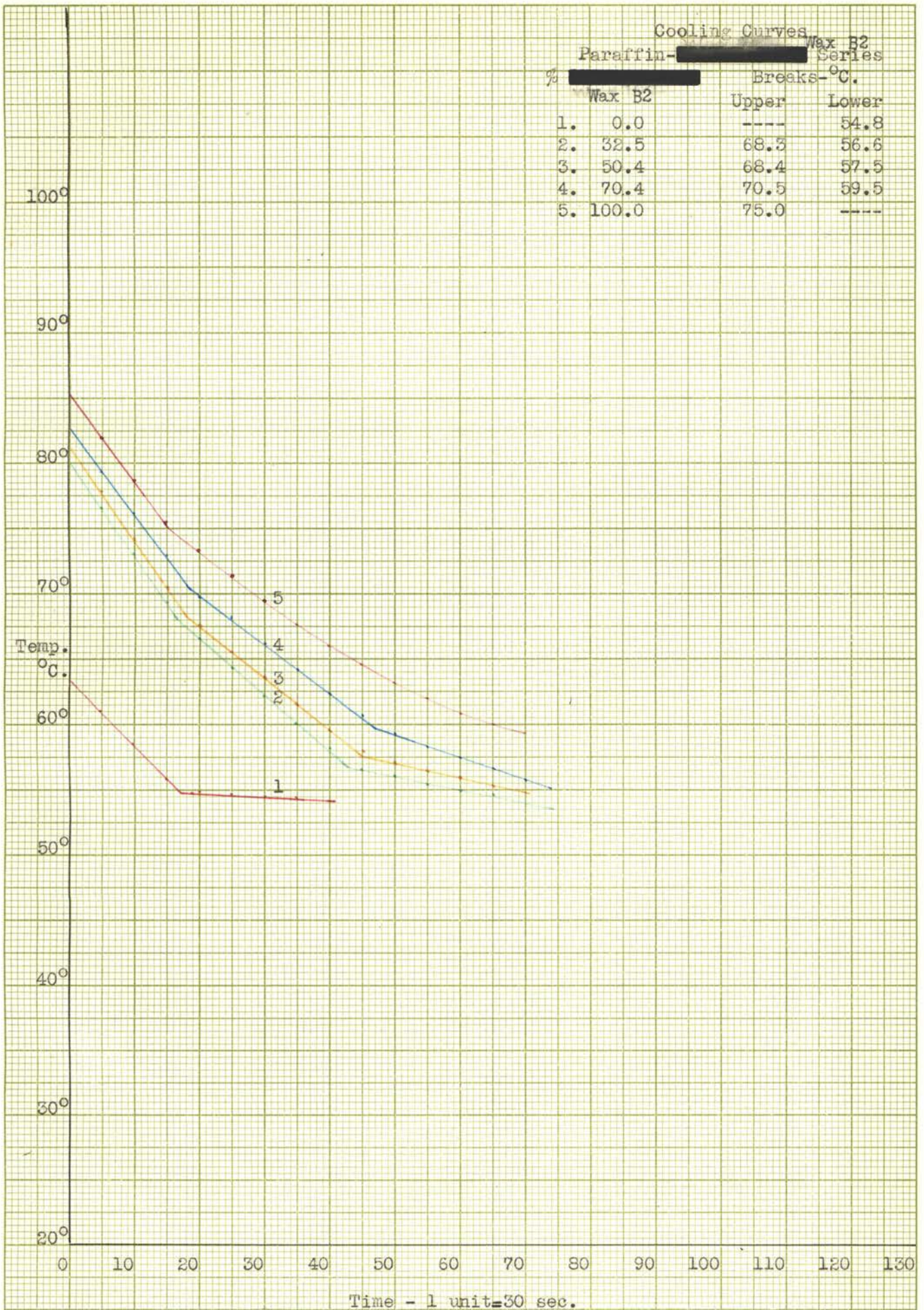


Time - 1 unit=30 sec.

Fig. 9.

Cooling Curves

Series	% Wax B2	Breaks - °C.	
		Upper	Lower
1.	0.0	----	54.8
2.	32.5	68.3	56.6
3.	50.4	68.4	57.5
4.	70.4	70.5	59.5
5.	100.0	75.0	----



Time - 1 unit=30 sec.

Fig. 10.

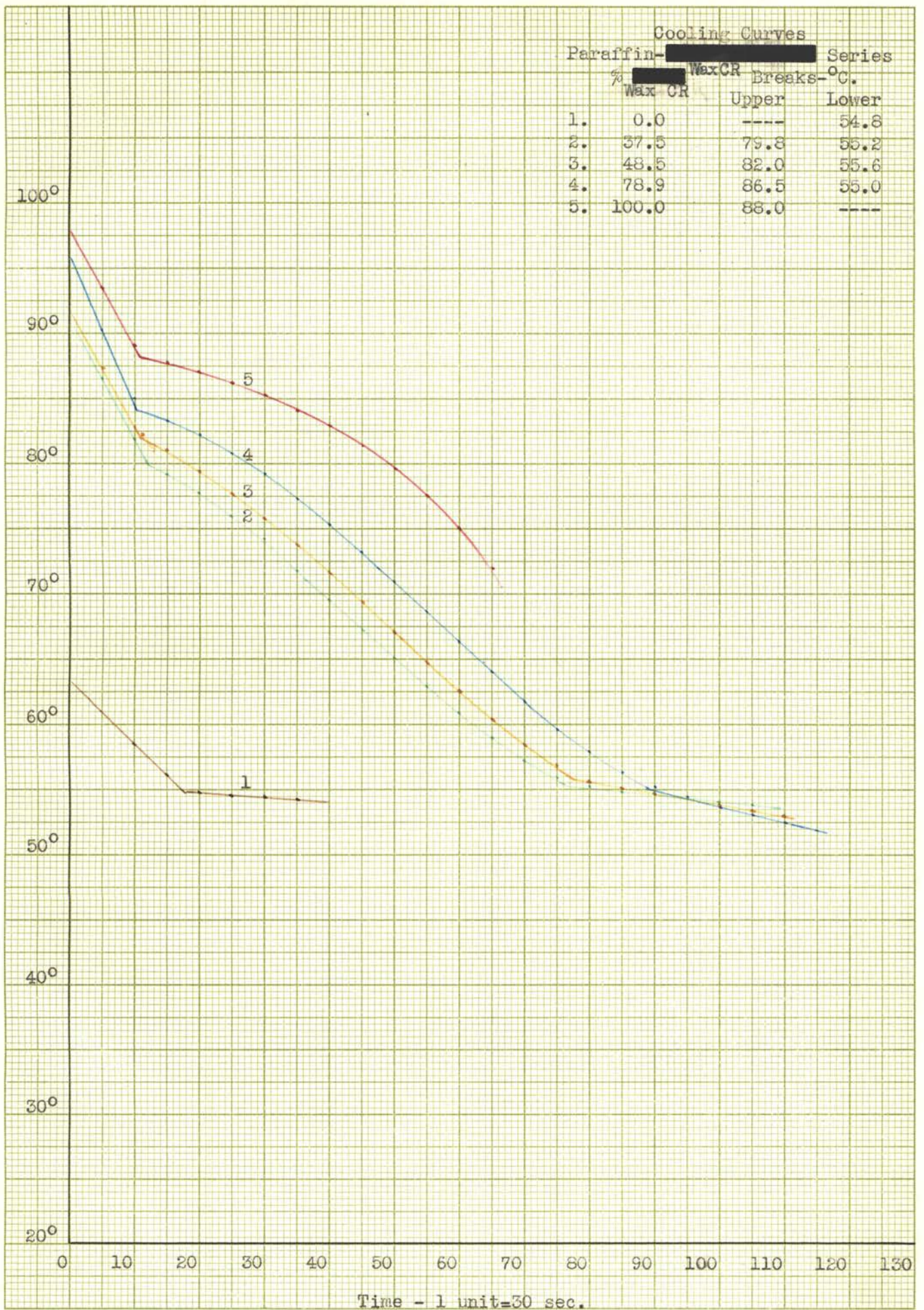
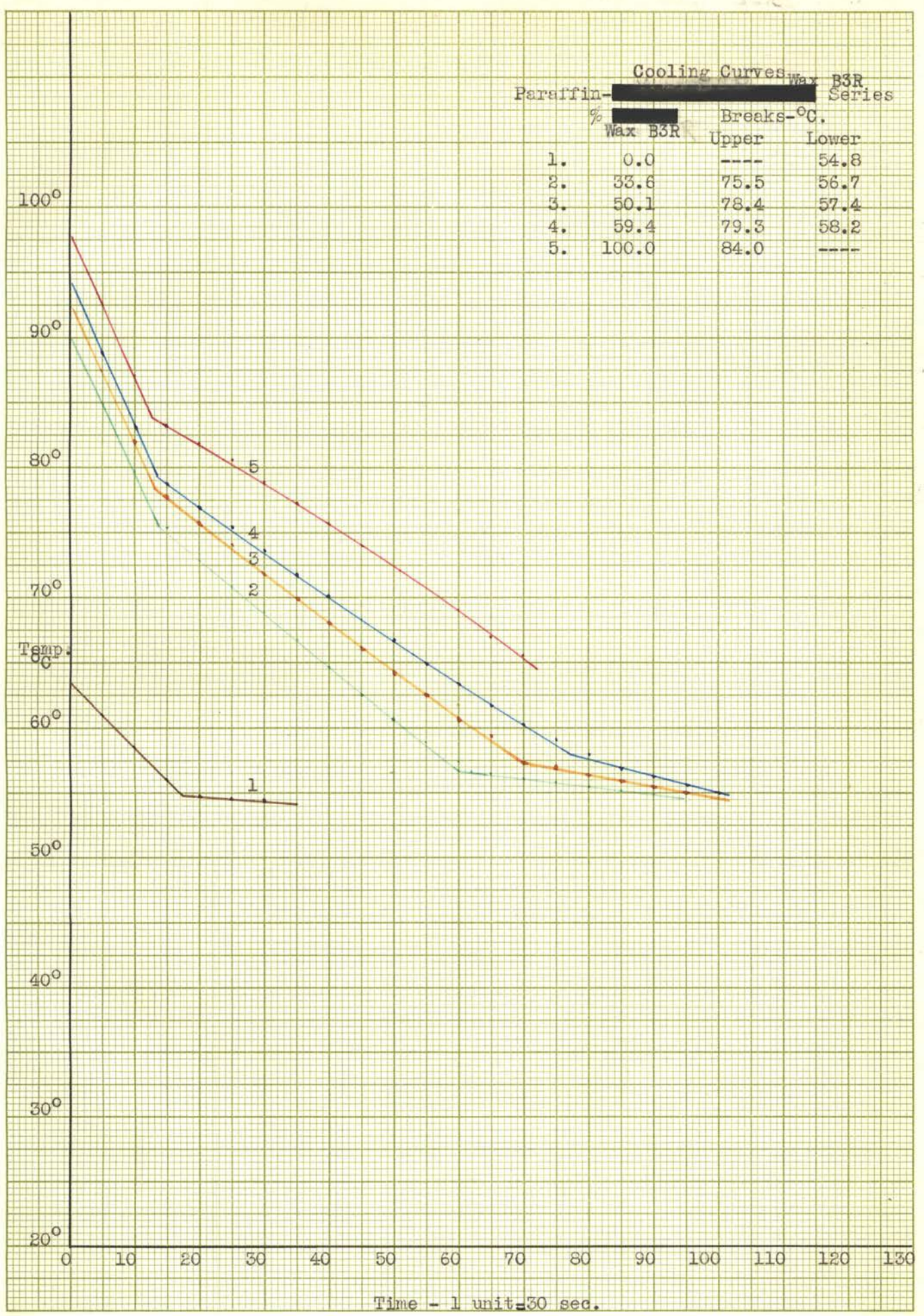


Fig. 11.

Cooling Curves - Wax B3R Series

Paraffin- % Wax B3R	Breaks-°C.	
	Upper	Lower
1. 0.0	----	54.8
2. 33.6	75.5	56.7
3. 50.1	78.4	57.4
4. 59.4	79.3	58.2
5. 100.0	84.0	----



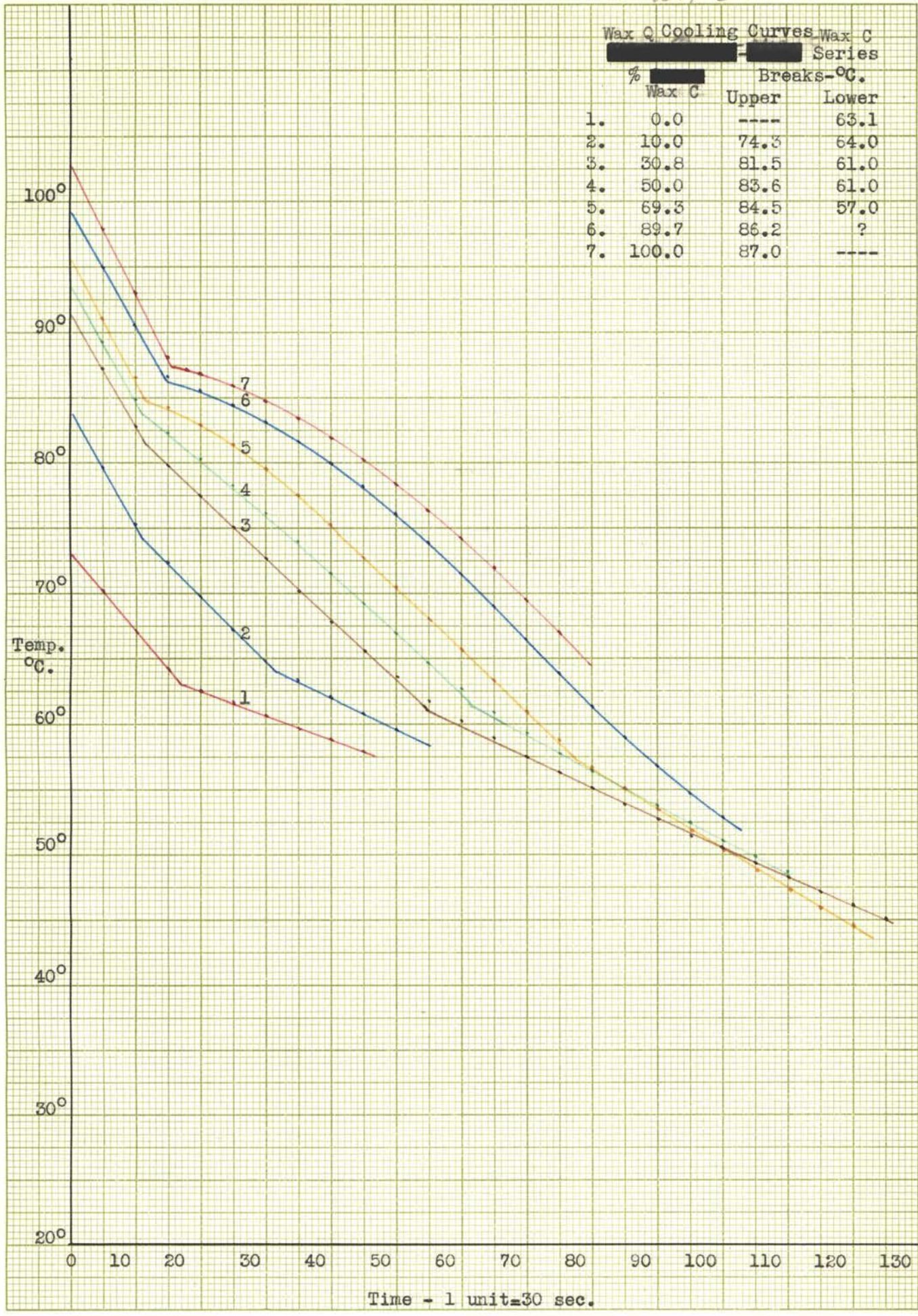
Time - 1 unit = 30 sec.

Fig. 12.

% Wax C

Wax Q Cooling Curves Wax C

Series	% Wax C	Breaks-°C.	
		Upper	Lower
1.	0.0	----	63.1
2.	10.0	74.3	64.0
3.	30.8	81.5	61.0
4.	50.0	83.6	61.0
5.	69.3	84.5	57.0
6.	89.7	86.2	?
7.	100.0	87.0	----



Time - 1 unit=30 sec.

Fig. 13.

Wax Q	Cooling Curves	Wax B2
Wax B2 %		Series
1.	0.0	63.1
2.	24.7	65.8
3.	52.4	72.5
4.	74.8	74.5
5.	100.0	75.0

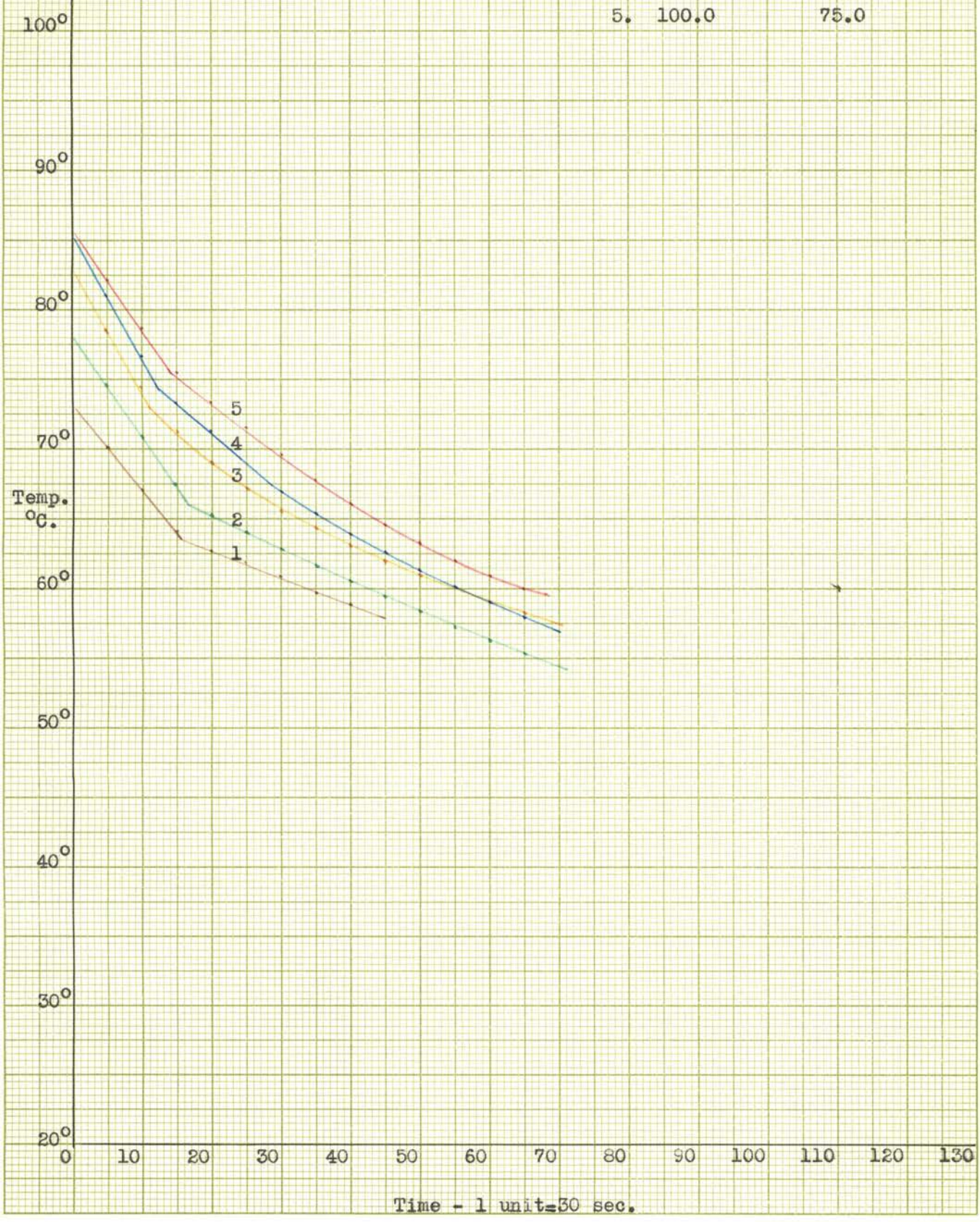
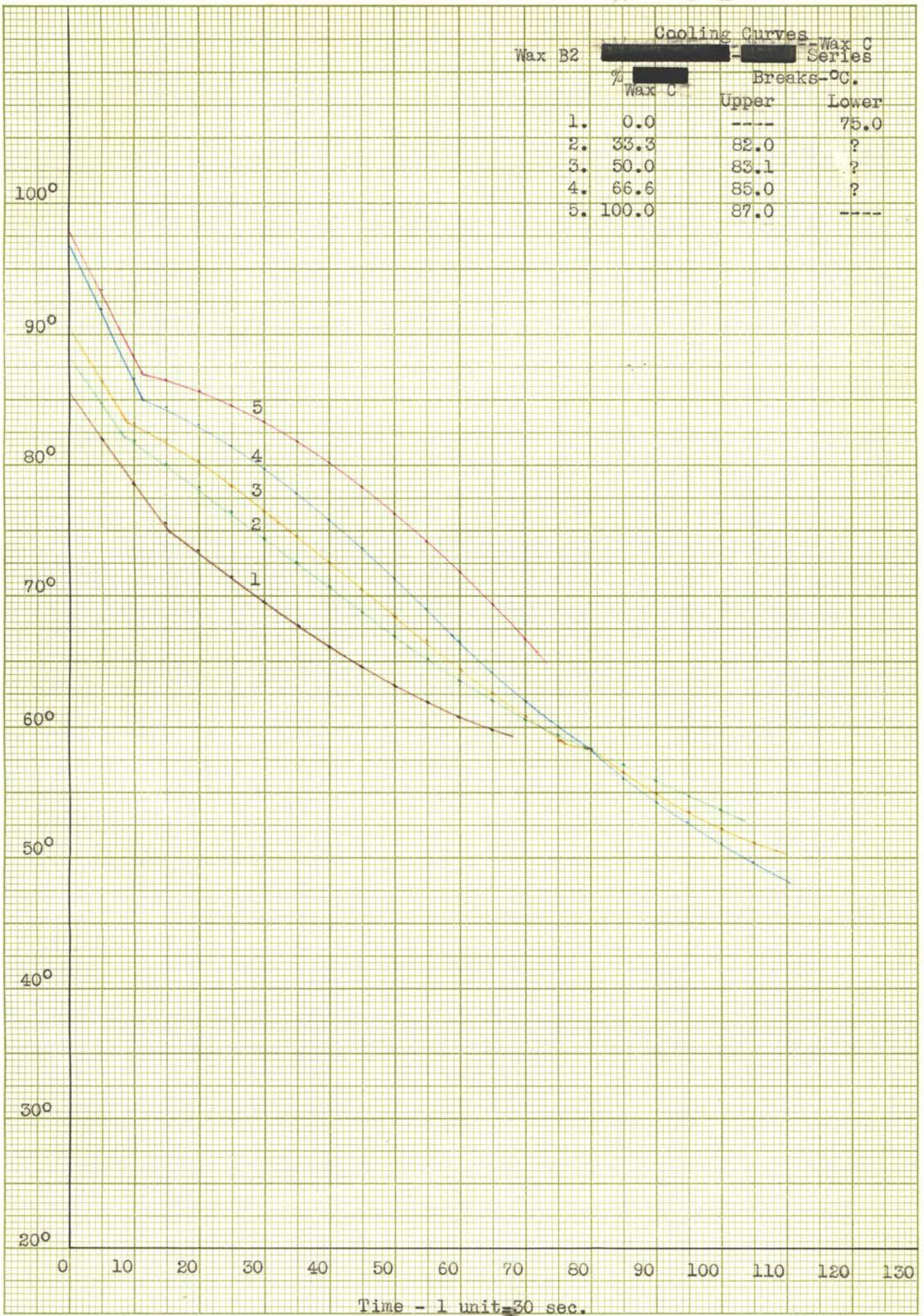


Fig. 14.

1/1 Wax C



Wax B2	Cooling Curves		Wax C Series	
	% Wax C	Breaks-°C.	Upper	Lower
1.	0.0	----	75.0	----
2.	33.3	82.0	?	----
3.	50.0	83.1	?	----
4.	66.6	85.0	?	----
5.	100.0	87.0	----	----

Time - 1 unit = 30 sec.

Fig. 15.

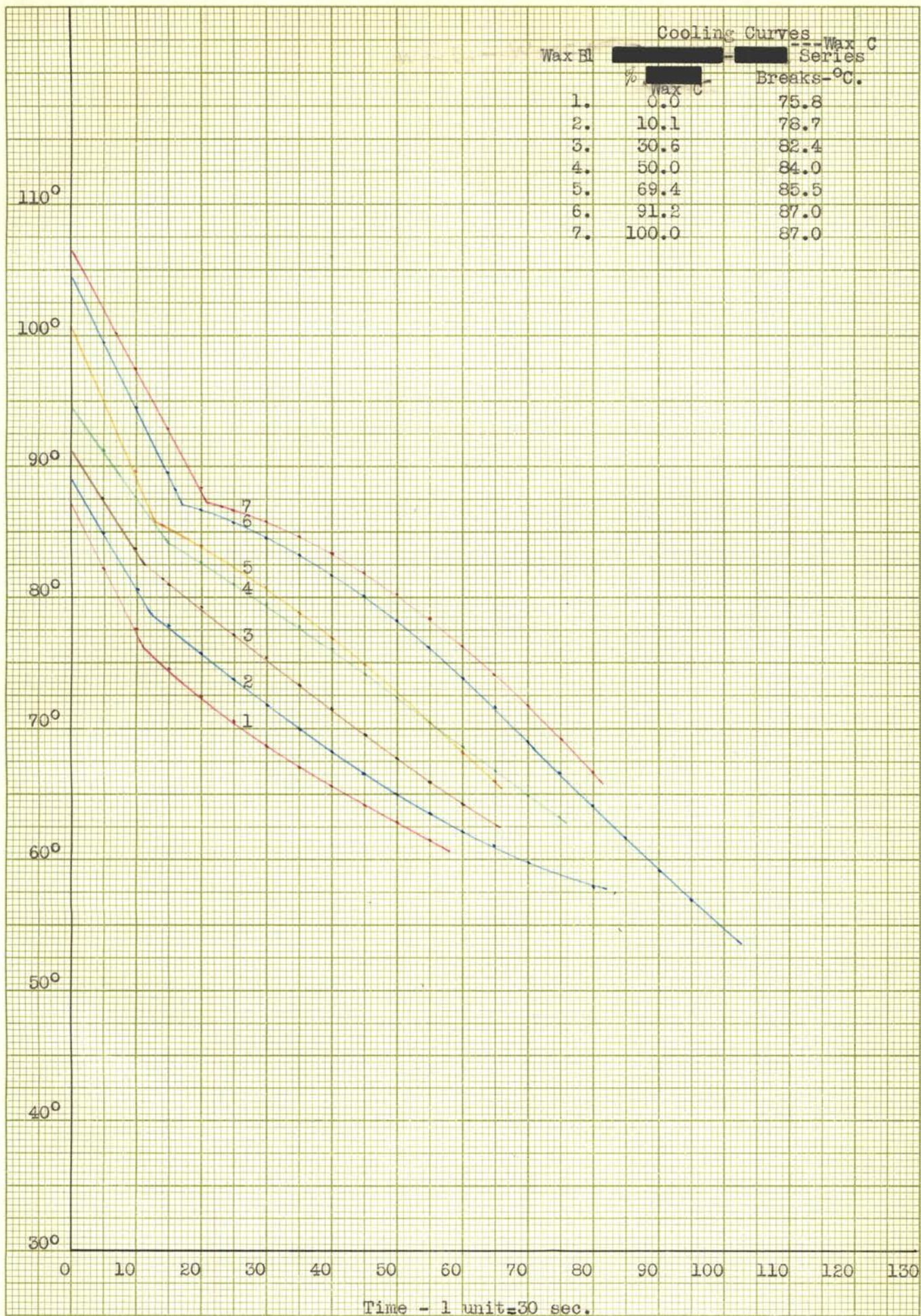


Fig. 16.

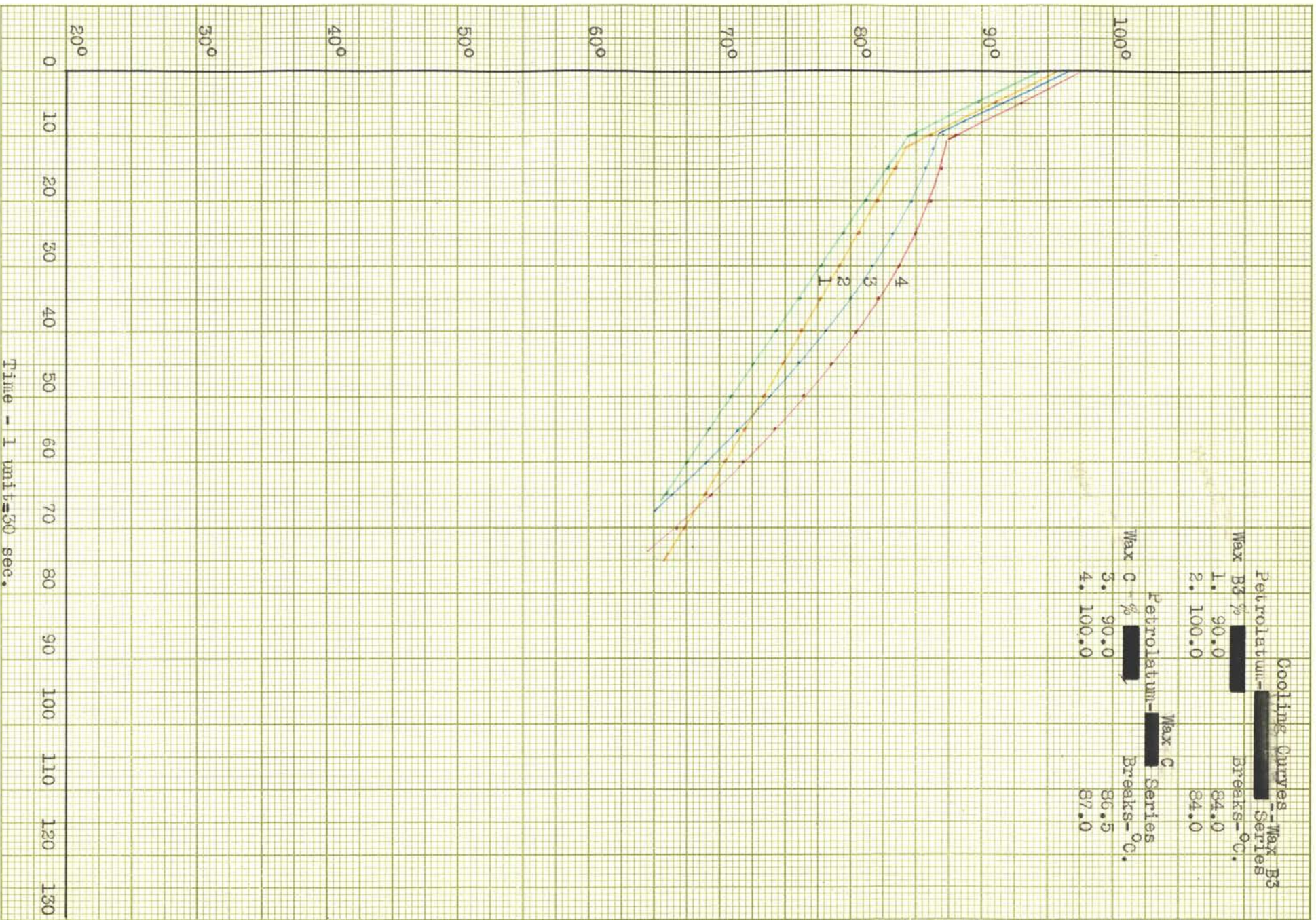


Fig. 17.

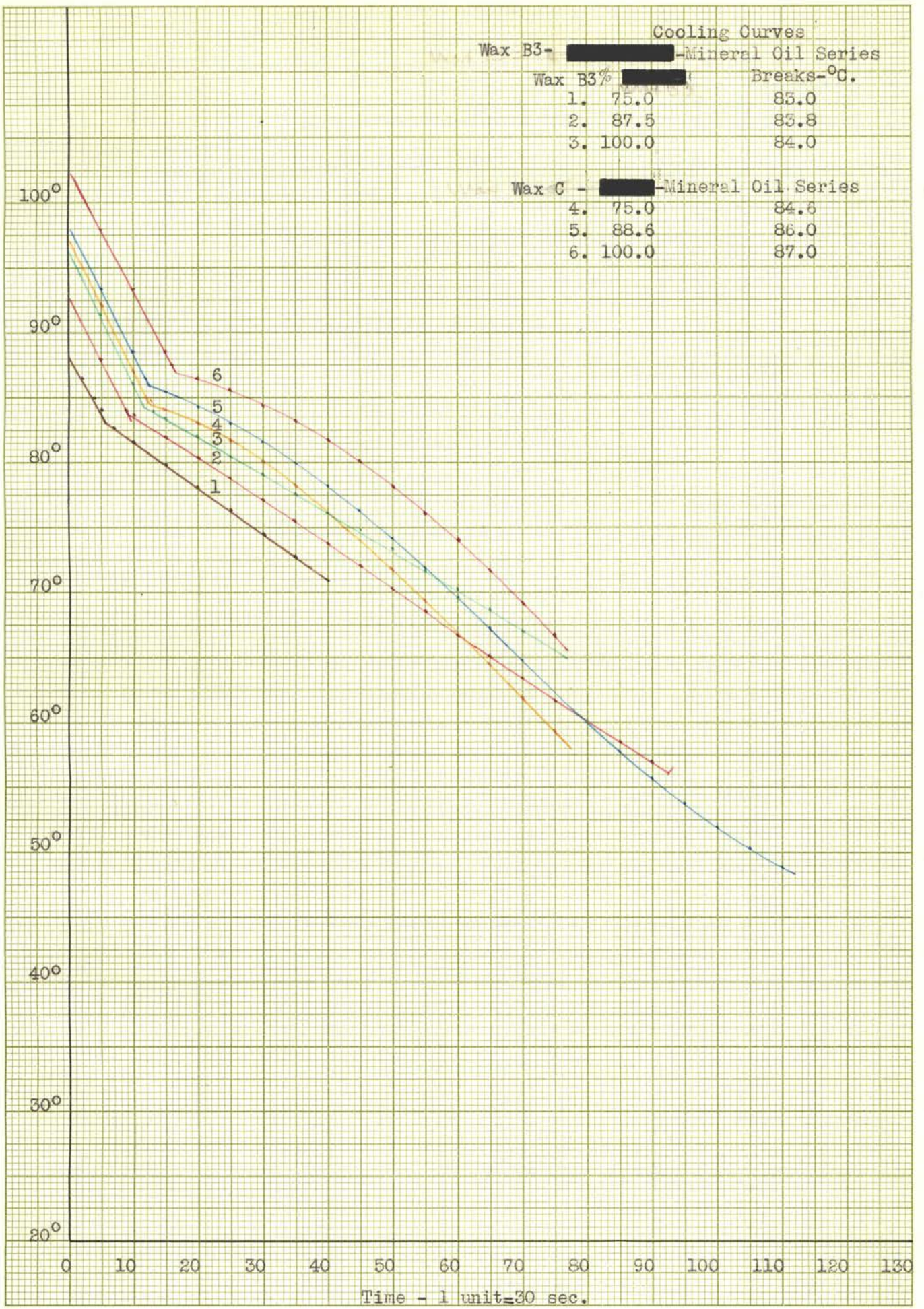


Fig. 18.

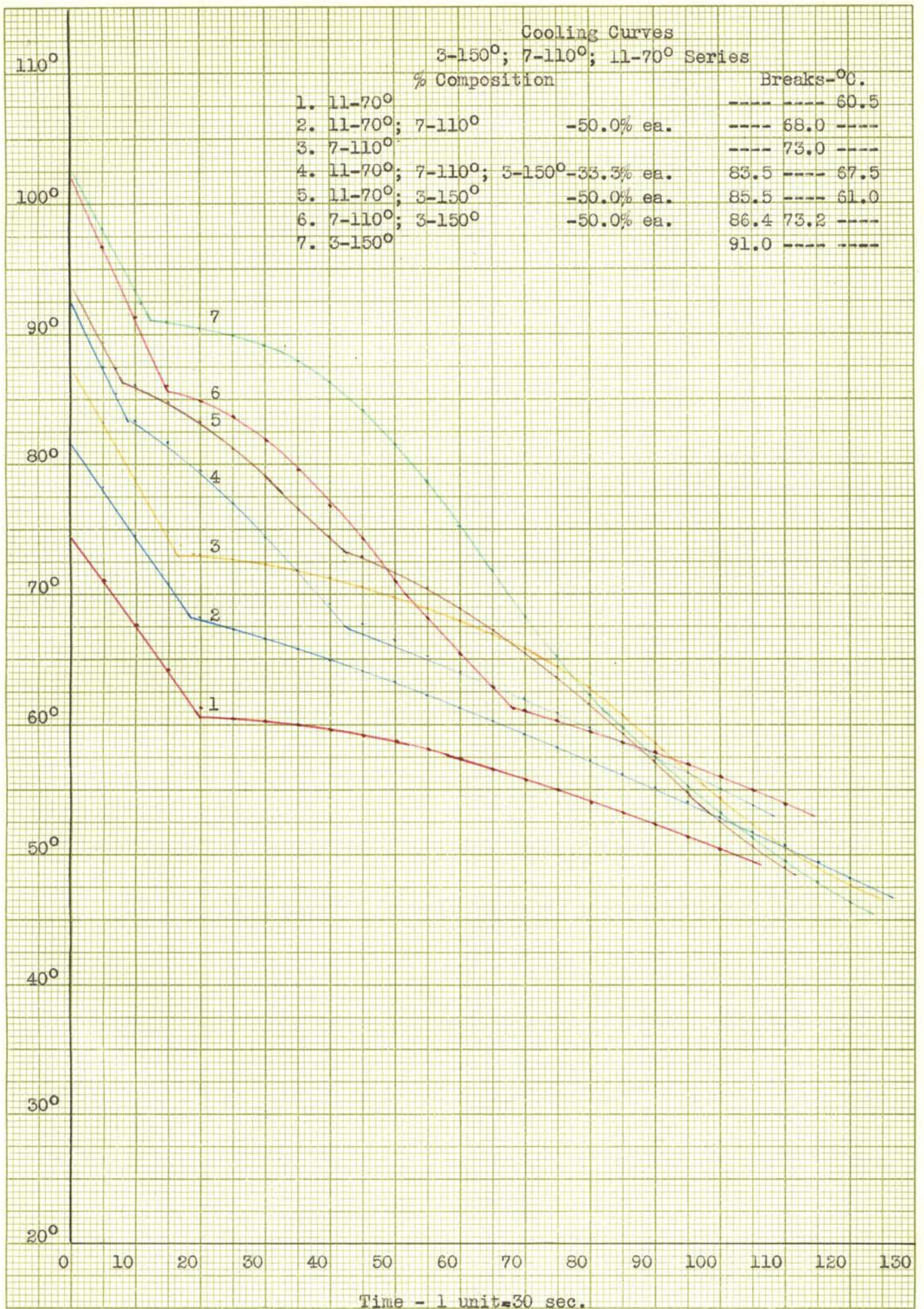


Fig. 19.

highest temperature show two breaks (Curves 5 and 6). Finally, the blend of all three fractions shows two breaks, not three as might have been originally expected (Curve 4).

So far as the data here imply, the three fractions do not show that they are of similar molecular make-up as one would expect from the fact that each comes from the same wax. If they were of the same molecular pattern, they should readily build into the same unit cells in the crystals giving a curve with a single break. If they did behave in this way, it would indicate the formation of solid solutions in which form these fractions existed in the original wax.

Fraction 3-150°, whose initial freezing-point is 18°C. higher than that of 7-110°, and 30.5°C. higher than that of 11-70°, gives a second break in the cooling curve when blended with either or both of them. Fraction 7-110°, whose initial freezing-point is 12.5°C. higher than that of 11-70°, does not give a second break when blended with the 11-70°. Then there is the fact that a third break does not appear when the three fractions are blended, as it should if 11-70° were freezing out separately. It may well be that enough of 7-110° still remains liquid when the initial freezing-point of 11-70° is reached, that its molecules can build into the crystal cells which are forming at that time to give solid solutions. This would not permit any break at this point.

This hypothesis then is capable of explaining the double breaks in cooling curves found when waxes which are quite unlike in molecular composition and melting-point cool and crystallize. It also explains the lack of a second break in cooling curves of waxes when

a series of different compounds of overlapping melting-points are present. An extensive examination of numerous blends of fractions prepared from the same wax is distinctly in order. If carried far enough it might serve to block out the melting ranges of wax fractions rather definitely.

The mutual effect displayed by waxes in the various blends upon initial freezing-points (as shown by cooling curves) are of interest. They are presented graphically in Figures 20, 21, and 22. Special attention must be called to the fact that the initial melting-point of Wax C is lowered by Paraffin Wax blended with it and likewise the initial melting-point of Paraffin Wax is lowered by Wax C. This effect is different from that found with all of the other blends examined.

Lowering of the Initial Freezing-Point
of Various Waxes by Paraffin

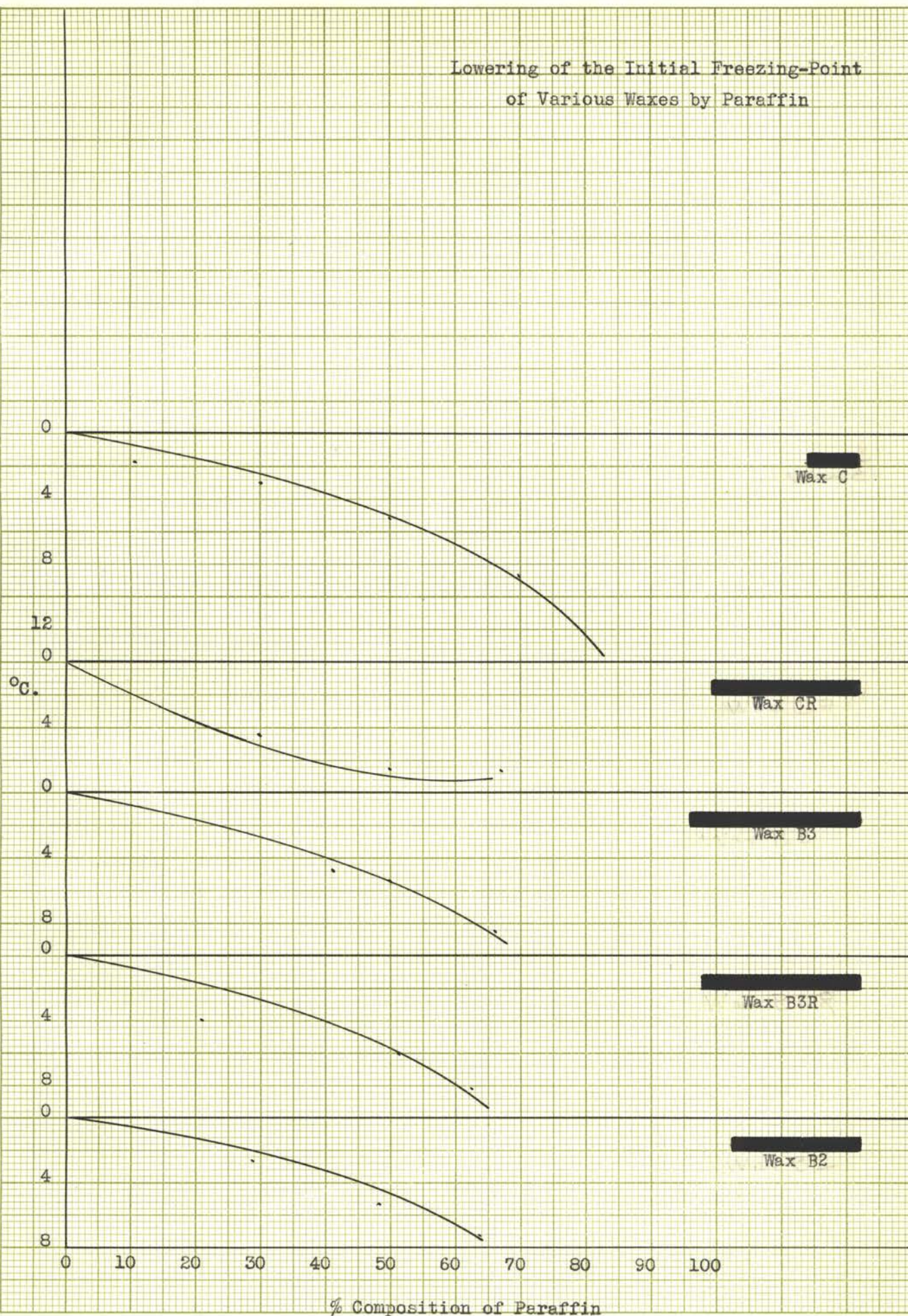


Fig. 20.

Lowering of the Initial Freezing-Point
of Paraffin by Various Waxes

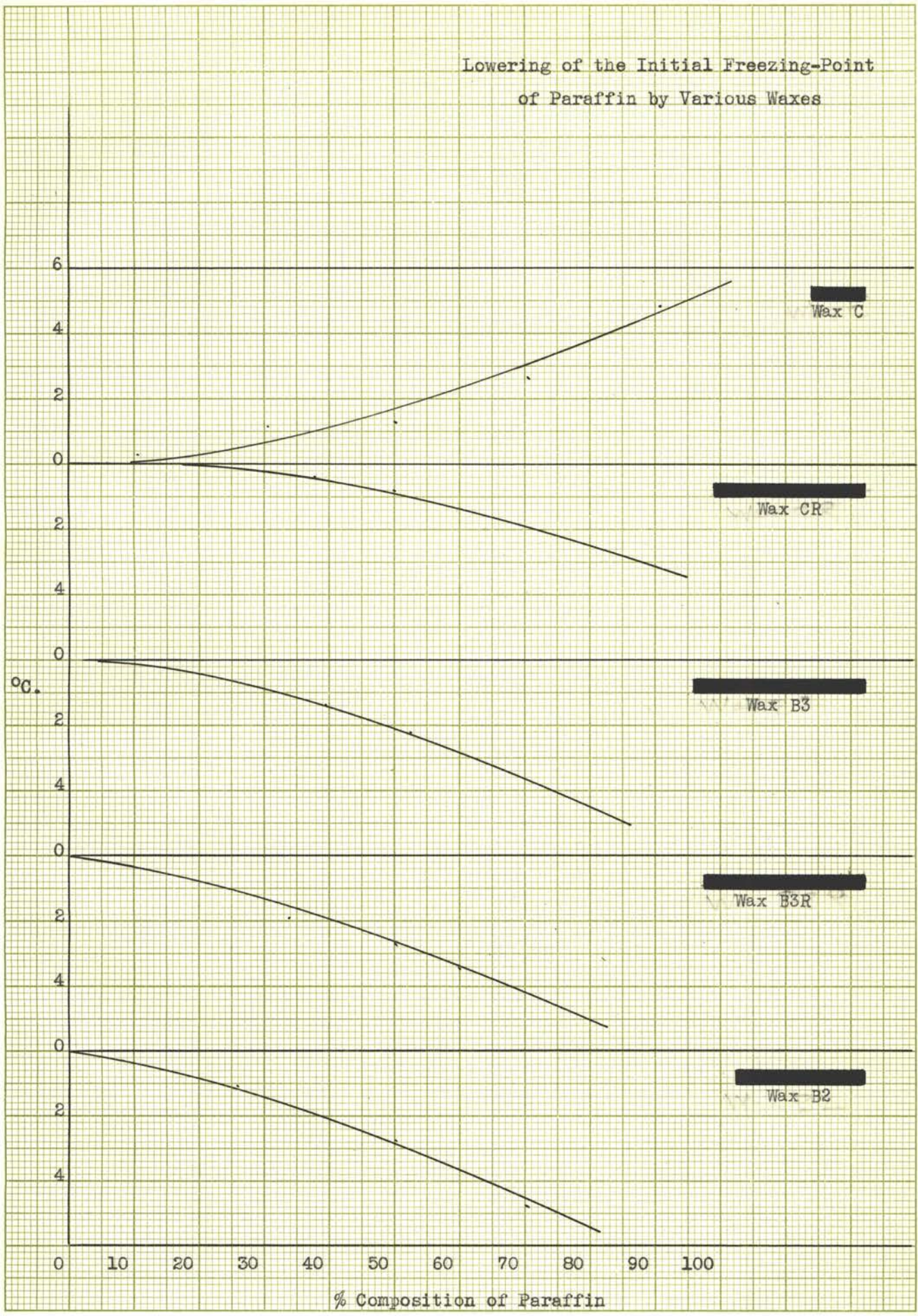


Fig. 21.

Lowering of the Initial Freezing-Point
in Various Blends of Waxes

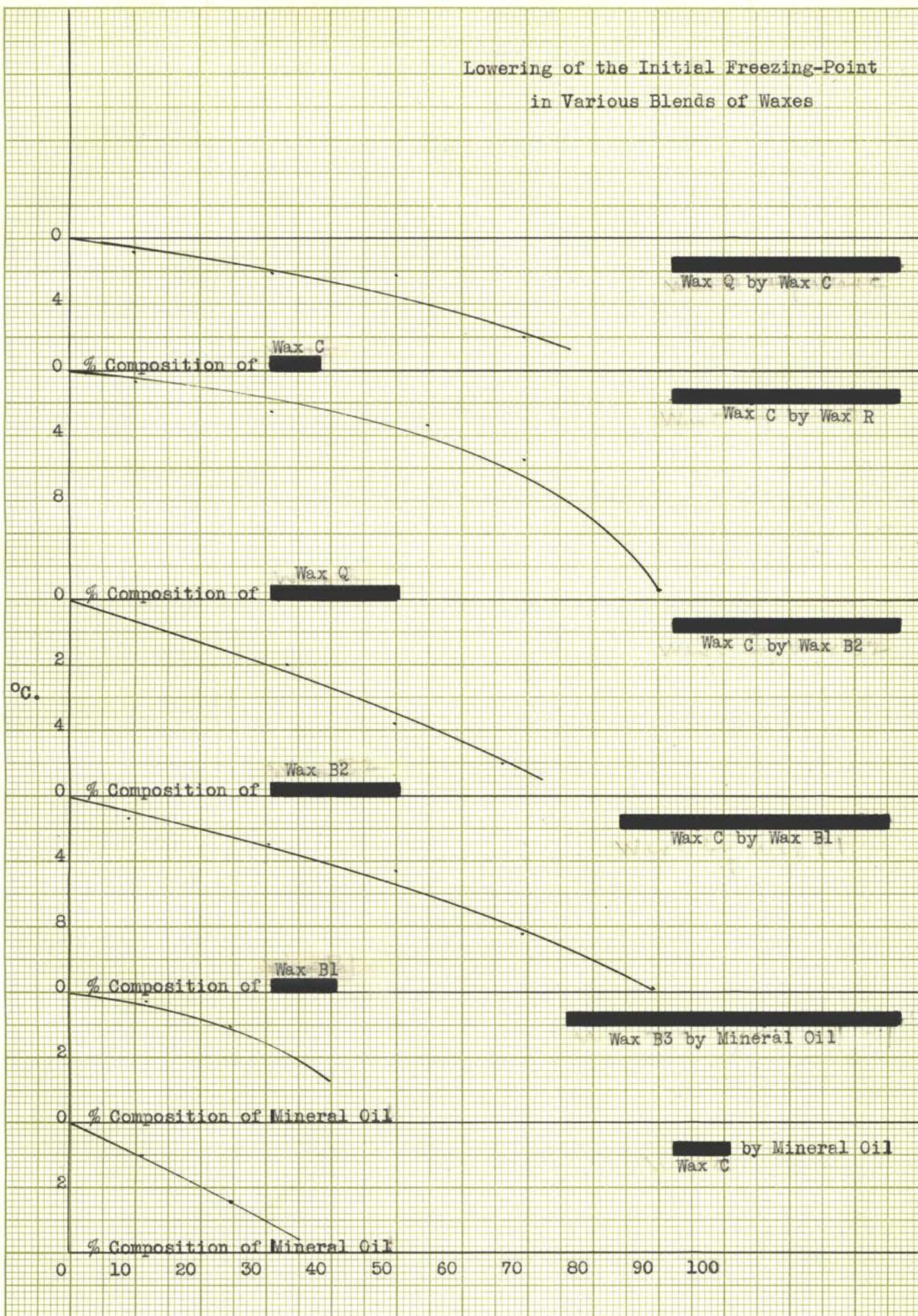


Fig. 22.

CONCLUSIONS

The dilatometric method can be used to determine the densities of waxes from room temperature to well above the melting-point. The accuracy of this method is approximately $\pm 0.5\%$. These determinations are very time-consuming and hence not well suited to commercial laboratory processes. Some waxes are exceedingly slow in attaining volume equilibrium. Densities of such waxes must therefore be considered as uncertain. Aside from these difficulties, the method has proved quite satisfactory.

Density-temperature curves obtained for commercial microcrystalline waxes or simple fractions of them are similar to the curves of paraffin waxes in the literature. Some blends of these waxes show not one but two breaks in the density-temperature curves; therefore, we conclude that there are two freezing-points in these blends.

Crystallinity Index as used for characterizing waxes has a sound foundation in theory. We found that crystallinity indices fail to place some of the waxes in their proper categories. This makes further work necessary before the method is acceptable.

Cooling curves serve to determine the initial freezing-points of microcrystalline waxes fairly satisfactorily. They do not give the sharp breaks desired in all cases. These curves frequently show two breaks as do the density-temperature and the enthalpy-temperature curves. Therefore, the determination of cooling curves can be used to explore waxes for the existence of two freezing-points. Cooling curves can hardly be used in characterizing wax.

The occurrence of two freezing-points when waxes cool is tentatively explained as being due to the freezing of one component while the other remains liquid; then, on further cooling, the freezing of the second component starts. This hypothesis still requires careful experimental confirmation.

BIBLIOGRAPHY

1. Bennett: "Commercial Waxes", Chemical Publishing Co., Brooklyn, New York, 1944.
2. Buchler and Graves: Ind. Eng. Chem., 19, 718-24 (1927).
3. Bureau of Standards, III, 189, D87-42.
4. Carpenter: Inst. Petr. Techn., 12, 56, 288, 313 (1926).
5. Clark: Nature, 120, 12 (1927).
6. Clark and Smith: Ind. Eng. Chem., 23, 697 (1931).
7. Ferris, Henderson, and Cowles: U. S. 1,937, 518 (1933); Ind. Eng. Chem., 21, 1090 (1929); 23, 681 (1931).
8. Francis and co-workers: J. Chem. Soc., 121, 1530 (1922).
9. Francis and Piper: "Science of Petroleum," II, Oxford University Press, London, England, 1938, p. 1205.
10. Francis, Piper, and Malkin: Proc. Roy. Soc., 128, 228 (1938).
11. Gruse and Stevens: "The Chemical Technology of Petroleum," 2nd. Edition, McGraw-Hill Book Co., New York, 1942, p. 574.
12. Gurwitsch: "Erdolverarbeitung," 1924, p. 384.
13. Hoiberg: Ind. Eng. Chem., 14, 323 (1942).
14. Kinsel and Phillips: Ind. Eng. Chem. Anal. Ed., 17, 152 (1945).
15. Krafft: Ber., 40, 4779 (1907).
16. Krafft and Weilandt: Ber., 29, 1323 (1896).
17. Mabery: Am. Chem. J., 19, 419 (1897); Proc. Amer. Acad., 37, 565 (1902); Am. Chem. J., 33, 251 (1905); Ind. Eng. Chem., 15, 1233 (1923).
18. Marcusson: Chem. Ztg., 38, 73 (1914); 39, 581, 613 (1915).
19. Padgett: "Science of Petroleum," III, Oxford University Press, London, England, 1938, p. 1942; Petr. Eng., 2, 80 (1931).
20. Padgett, Hefley, and Henriksen: Ind. Eng. Chem., 18, 832 (1926).

21. Piper, Brown, and Dymont: *J. Chem. Soc.*, 127, 2194 (1925).
22. Reilly and Rae: "Physico-chemical Methods", I, D. Van Nostrand Co., Inc., New York, 1939, p. 465.
23. Sachenen, Zherdeva, and Vasilyev: *Nat. Petr. News*, 23, 49 (1931).
24. "Standard Methods", The Institute of Petroleum, London, England, 4th. Edition, 1943, p. 259.
25. Ward, Kurtz, and Fulweiler: "Science of Petroleum", II, Oxford University Press, London, England, 1938, p. 1137.
26. Williams: *Analyst*, 66, 3 (1941).
27. Wilson and Downer: "Science of Petroleum", II, Oxford University Press, London, England, 1938, pp. 1433-7.
28. Wood and Brusie: *J. Am. Chem. Soc.*, 65, 1891 (1943).
29. Zaloziecki: *Z. angew. Chem.*, 2, 261, 318 (1888): original, *Dinglers polytech. J.*, 267, 274 (1888).

AUTOBIOGRAPHY

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