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A Study of Technical Possibilities of Vulcanized Oil Compositions

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A STUDY OF TECHNICAL POSSIBILITIES OF VULCANIZED OIL COMPOSITIONS

A thesis submitted by

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INTRODUCTION AND HISTORICAL

Factice is produced by the vulcanization of raw or blown glyceride oils. The public seems to be almost entirely unfamiliar with factice, although it is an important industrial material. It was known before rubber was introduced into Europe (1), and is used in the familiar form of "Artgum." Though well known to industry, it has apparently been independently rediscovered by many inventors. The rubber-like properties of factice are such that, in the trade, it is often known by the name "rubber substitute" (1). The entire field is reviewed by Whalley (24).

Factice is usually produced by the action of sulfur or sulfur chloride on any one of a great number of oils: rape, castor (2), colza (2), linseed (2), grapeseed (3), soybean (4), cottonseed (5), herring (6), saradine (6), corn, tall, or poppy seed (1). Commercially, factice is manufactured in two distinct types. Brown factice is made by the treatment of oils with sulfur at 160° to 200° C. (2); the soft kinds, containing a low sulfur content, are prepared from highly blown oils; harder varieties are made from raw oils and may contain up to 20 per cent of sulfur. Such a factice may contain 1 to 8 per cent of free sulfur and has a deep reddish-brown color. White, or light, factice is prepared by the cold vulcanization of an oil with sulfur monochloride; rape, colza, and corn oils are favored for this purpose. The quantity of sulfur chloride used may be as high as 25 per cent of the weight of the oil. Benzine or mineral oil may be added to prevent overheating after the addition of the sulfur chloride; chalk or alkaline solutions are employed to neutralize the free acids formed. Its free sulfur content should not exceed 0.5 per cent (7). Another form of factice is made by treating a warm oil with a definite quantity of flowers of sulfur and completing the vulcanization with sulfur chloride. This product has fairly good mechanical properties.

Esch (8) prefers to classify a factice according to its chemical structure rather than by its method of preparation or color. He contends that, in place of the type classification just presented, there are four fundamental factice types based on various proportions of combined sulfur and in different modes of combination. Furthermore, two other types exist, depending on whether the oil is oxidized before or after the treatment with sulfur or sulfur chloride.

Several other polymerized materials have been termed "factice," although their method of preparation is entirely different from those described above. Hock (9, 10) has produced an oil product ("Voltol") resembling factice by the treatment of fish oil or rapeseed oil with the silent electric charge. Rheinberger (11) applied the term "factice" to an elastic composition composed of sulfite liquor and dissolved cellulosic material (for example, waste paper dissolved by the aid of sodium silicate). Materials such as casein, latex, blood, solid rubber, cork, or wood flour may be added. These are, of course, special cases and are quite different from the usual concept of the meaning of "factice."

Physically, factices are solid jellies, ranging from light white or yellow to deep red or red brown in color. They are insoluble in rubber solvents but swell to form very dilute gels. They are saponified by treatment with alkalies or even steam or hot water. Although factice has many rubber-like properties, it has never been produced with properties which can meet the tests of resiliency, extensibility, toughness, and resistance to temperature changes shown to be necessary for a general rubber substitute. Factices, in general, are highly grease and water resistant and for these reasons may find applications where they are more satisfactory than rubber.

For nearly 100 years factice has been used principally as a compounding agent with either natural or synthetic rubber (1). In recent years the tendency has been to regard factice less as a substitute and more as a definite compounding material introduced to improve aging and to produce a good effect in the mechanical working of rubber stocks. It does not oxidise or become resinous, and shows no inclination to ropiness in spreader stock, as well as restraining blooming (2). Brown factice is used in hot-cured mixings, whereas the white variety finds application in cold-cured mixings. Factice has many applications as an adulterant of reclaimed rubber and of gutta-percha. Certain factice compositions are employed as substitutes for the latter (12). The smooth feel in rubber proofings is obtained by the compounding of factice material. Grease resistance of rubber goods is improved in the same way. Because this vulcanised material possesses some of the characteristics of rubber, it is employed in the manufacture of insulated wire, druggists' sundries, erasers, stationers' goods, and other products. Even when incorporated in vulcanised rubber in large amounts, it does not destroy the "rubbery" character of the product although it does lower the tensile and abrasion resistance. When used in colored tiles, it prevents curling and stops degradation of the pigment tint. Its presence in tubing stocks aids smooth extrusion. Of course, one of the marked advantages of compounding with factice materials is the low cost of the mixings. The use of factice alone is very minor, although Artgum is a familiar factice product.

Much work has been done on the vulcanization of all types of oils. However, in almost every case the material was desired for use as a rubber substitute or as a compounding material. Esch (8), Kaufmann (13), Salchow (14, 15) and many others have studied the chemical composition of factice in an attempt to explain its structure and the process of vulcanization. Others, like Grandel & Company (16), have developed chemical and physical methods for the evaluation of such materials. From the available literature, it would seem that the pulp and paper industry offers an entirely new field for the application of factice or factice-modified materials. Only two instances were found where factice materials had been applied to papers. Rydberg (17) obtained a patent for producing a vulcanized fiber material by impregnating board with a special oil and about 75 per cent of the sulfur chloride necessary for complete vulcanization; addition of the remainder of the sulfur chloride after impregnation completed the vulcanization. Kaye (18) in 1926 patented a process for emulsifying oils in a warm alkaline solution and adding latex and a vulcanizing agent, such as alkali or alkaline earth sulfides or polysulfides. These treated oils were coagulated with aluminum sulfate and were suggested for beater sizing or coating operations. Evidently neither of these processes proved successful; at least, they are not in use at present. Hence, it would seem that the opportunity still exists to find a practical use for factice materials in the paper industry.

PRESENTATION OF THE PROBLEM

The current scarcity of the usual canning and packaging materials has brought about an acute need for special types of wrapping and packaging papers. At present, the demand for a cheap, available, large tonnage wrapping paper for commercial and military use is ranked as one of the important problems of the war. If it were possible to find a material or group of materials which would fill any one of the present needs, such a product would be considered a contribution to the war effort.

It was the purpose of this investigation to discover a product which would be useful for wrapping and packaging the many types of materials needed for commercial and military consumption. Ideally, a product is desired which is both grease resistant and resistant to water and water vapor. However, a film which would do either of the jobs well would be a marked improvement. In the search for such a product, the following specifications were set:

1. The product must be satisfactory from the standpoint of grease resistance or resistance to water and water vapor.
2. The sheet must be flexible and withstand folding and flexing over a wide temperature range (-40° to 200° F.).
3. The materials employed in the preparation of the product must be available, preferably cheap, and abundant even under the war conditions.
4. If possible, the material had to be such that existing laminating equipment could be used in the manufacturing operation.

Previous work at The Institute of Paper Chemistry (begun by Wink (19) on castor oil and extended by Rowley (20) on linseed oil) indicated very favorably the possibility of forming a factice material which could be incorporated into a sheet of paper, thereby giving it the qualities mentioned. The factice material might be formed into a continuous film between two sheets of kraft paper which could be laminated, giving a highly grease- and water-resistant product. Or, it might be that a sheet of paper could in some way be impregnated with factice material, thus securing the same effect.

Several difficulties had to be overcome before such a process could be carried out. Factice material as produced by the vulcanization of oil had several disadvantages. The completely vulcanized oil was so rubbery, gummy, and tacky after cooling that it presented mechanical problems. In this form it was difficult to handle, and films prepared from it contained numerous pinholes. If hot application was tried, the vulcanization process proceeded until the factice became so still and crumbly that it was impossible to form continuous films. In the early work, no low temperature accelerators were found which would favor the vulcanization reaction at temperatures or time intervals which were not harmful to the paper. Therefore, it seemed rather impractical to impregnate a sheet with partially vulcanized oils and then heat-treat the sheet to cause further vulcanization of the oil.

The first problem to be solved was the production of a factice from linseed or other oils which could be formed into a continuous film. Once the film had been prepared, it had to be investigated with respect to the four objectives outlined above. The modification of the factice film by the addition of thermoplastic waxes or resins was worthy of investigation, from the standpoint both of obtaining desirable qualities and of reducing the cost of the material. Later it was found that, even though continuous factice films could be formed, they did not possess good water-vapor resistance. Modification of the factice film to produce such resistance had to be investigated. Later in the investigation it seemed advisable to study the possibility of using factice as a plasticizer for waxy or resinous materials.

After the most promising material had been selected from the group of products made, a more complete study of the variables involved in the production of the material had to be carried out. Methods of plant control and operations had to be investigated, as well as actual semicommercial production methods and commercial applications.

PART I

AN INVESTIGATION OF FACTICE AND FACTICE FORMATION

GENERAL METHOD OF FACTICE PREPARATION

It was found possible to vulcanize a water emulsion of linseed oil at a temperature of 100° C., and then incorporate the factice on or between paper sheets. This involved long cooking times, and the factice obtained did not possess many qualities desirable for the work; therefore, the method was discarded. A much simpler procedure for the preparation of a brown factice involved the treatment of an activated oil with flowers of sulfur at higher temperatures. Factice made in this manner could be prepared in a reasonable length of time and was suitable for laminating purposes. The general method of preparation was standardized and was carried out as follows.

Thirty grams of previously activated oil were weighed into a 100-ml. beaker. The oil had been activated by one of the several methods which will be discussed later. The accelerator used in the greater portion of the investigation was a commercial vulcanizing compound (C-16) manufactured by the Vanderbilt Company. The water emulsion of sulfur, zinc oxide, Butyl zimate, and other materials was added to the cold activated oil in amounts varying between 5 and 10 per cent. This oil and water emulsion was then heated quickly over a Bunsen flame to 100° C. Care had to be taken since the boiling off of the water at this point caused bad foaming of the emulsion. The mixture was heated carefully until all the water had been driven off, and the temperature was finally raised to 145° C. The beaker was placed on an electrically heated and controlled hot plate, where the temperature was held constant at 145° to 150° C. A constant speed stirrer was placed in the oil to insure good mixing and to avoid local overheating. After the stirrer had been started, the desired amount of sulfur (5 to 15 per cent) was added and stirring was continued until factice formation took place. The time for factice formation was taken as the interval between the addition of the sulfur and the end of the reaction. The initial heating period for the removal of the water was about 1 minute, whereas the final cooking period required several minutes to several hours, depending upon the activity of the oil used.

The time to factice was a more or less arbitrary end point, yet a very definite one. After the addition of the sulfur, the liquid became deep red or reddish brown in color and there seemed to be little change in viscosity. Suddenly the liquid became very thick, viscous, and tacky so that it started to rotate with the stirrer and climbed up the rod. The end point was taken as the time at which the factice was so viscous it could be picked completely off the bottom of the beaker by the stirring rod. Variations in the end point of a certain oil were less than 1 per cent of the total cooking time. In the case of the less active oils it was slightly harder to determine the end point, because the viscosity of the oil increased more gradually. However, the factice time, or end point, was still very definite.

If a dry accelerator was used, it was unnecessary to remove water before heating the oil to 145° C. In these cases the oil was heated to 145° C., placed on the hot plate, and the dry accelerator and sulfur added together. Other conditions remained as before.

After the factice had been formed, two sheets of high density kraft paper were laminated by passing them through a horizontally supported clothes wringer, the hot factice being poured into the nip between the rolls.

A STUDY OF THE ACTIVATION PROCESS

Raw or boiled linseed oil can be vulcanized without any pretreatment, but the process requires a very long time and high percentages of sulfur. It would be necessary to heat a combination of linseed oil and sulfur a day or more before a thick factice would be obtained. However, it has been known for many years that, by means of a pretreatment or activation process, the activity of the oil is increased in a very few minutes. This activation process is accomplished by heating the oil to a high temperature. It is believed that, during this heating process, there is a shift in the unsaturated double bonds of the oil, producing conjugate double bonds which take part in the vulcanization process. It has been proposed that the sulfur adds to the conjugate double bonds and forms the linkage between the molecules. At the same time oxidation must take place. It is further believed that blowing accelerates the activation process, because blown castor oil proved to be much more reactive than the unblown oil.

In the first part of the experimental work, the linseed oil was activated by heating to a high temperature. It was found that, if 800 ml. of raw linseed oil were heated to 350° C. in about 2 hours, held at this temperature for approximately 30 minutes, and then allowed to cool to room temperature, the resulting oil was very reactive and would form a factice in 20 to 30 minutes using 5 per cent of both sulfur and accelerator (based on the weight of the oil). Several batches of oil were treated in this manner during the course of the investigation. Although this method of activation is the simplest and quickest for small quantities and laboratory use, it is far from being commercially feasible. In the first place, special heating equipment employing gas or direct heat would be necessary to reach and maintain this high temperature. Furthermore, the flash point of linseed oil is in this range and on several occasions the oil caught fire. Such a process would not prove too satisfactory in large-scale operations. The activation process also proceeded with such rapidity at this elevated temperature that it was very hard to control the activation and obtain a constant product.

If the activation of linseed oil were to be carried out on a commercial scale, a more feasible process had to be developed. At the same time, it was necessary to devise some method of plant control by which the activation process could be followed and controlled so that the finished oil possessed the desired degree of activity, as well as other requisite properties. In the preliminary activation processes it was noticed that the oil experienced a very definite change in color, viscosity, and other physical characteristics during activation. There was also a loss of about 8 to 10 per cent by weight in volatile materials. All of these facts seemed to indicate that viscosity, index of refraction, transmission of light, or other physical properties could be used as a quick, accurate indication of the activity of the oil.

Method of Activation

In order to study the activation process, a series of experiments was set up involving the three variables of time, temperature, and blowing. Because the previously used temperature of 350° C. was too near the flash point of the oil, it was decided to try activation at a lower temperature. In order to obtain the greatest quantity of useful knowledge from the fewest number of activation runs, it was decided to make one run at 300° C. without blowing and a run at 300° C. with continuous blowing. This would show the effect of aeration on the activation process. If aeration of the oil during activation accelerated the process to any great extent, it might be possible to lower the activation temperature to 200°.

Activation of Oils 300-310. A stainless steel bucket containing about 3 liters of raw linseed oil was heated on a 1000-watt hot plate to a temperature of 300° C. in 70 minutes. During the heating process, the oil was agitated by means of a stainlesssteel stirrer. The temperature of the oil was increased from 23° C. to 300° C. at the rate of 20° C. every 5 minutes. Occasionally it was necessary to heat the sides of the bucket with Bunsen burners in order to maintain the temperature schedule. The oil was sampled at the beginning of the process, at the time temperature was reached, and every 15 minutes thereafter. About 400-ml. samples were taken, allowed to cool to 100° C., and placed in small glass samples jars. In this manner it was possible to follow the physical and chemical changes taking place in the oil during activation. The data for many of these samples are given in Table I.

TABLE I

PROPERTIES OF ACTIVATED OILS

	Heat Treatment, min.						Factice Time, min.		
Oil	Temp. ° C.	Time to	Time at	Total	$n_D^{37.5}$	R.K.V. sec.	5% S	10% S	15% S
300	none	0	0	0	1.4739	5.9			
301	300	70	0	70	1.4750	6.7			
303	300	70	30	100	1.4762	9.5			
305	300	70	60	130	1.4783	17.4			
306	300	70	75	145	1.4792	27.1			
307	300	70	90	160	1.4812	48.1	250		
				With continuous blowing					
311	300	70	0	70	1.4757	9.1			
312	300	70	15	85	1.4780	14.1			
313	300	70	30	100	1.4800	26.6	260		
314	300	70	45	115	1.4830	101.2	62		
315	300	70	60	130	1.4350	352.3	13.5		
316	300	70	75	145	1.4873	1350	1		
				With continuous blowing					
211	200	30	0	30	1.4742	6.3			
212	200	30	30	60	1.4750	7.2			
213	200	30	60	90	1.4760	8.5			
214	200	30	90	120	1.4772	12.5			79
215	200	30	105	135	1.4780	15.2		145	55
216	200	30	120	150	1.4791	20.7		76	46
217	200	30	135	165	1.4800	27.3	265	62	41
218	200	30	150	180	1.4805	35.0	112	36	27
219	200	30	170	200	1.4812	55.8	59	26	15
220	200	30	190	220	1.4822	85.7	31	17	8.5
221	200	30	210	240	1.4834	125.6	17	12	7
222	200	30	230	260	1.4835	188.1	13	9	6
B	350	30	30	60	1.4872	549	60		
C	350	130	25	155	1.4854	324	20		
D	350	110	30	140	1.4870	550	60	25	
E	350	135	30	165	1.4845	235	30		
F	350	135	45	180	1.4928	1836			
Conjulin (commercial product)					1.4883	419	23	9	5

All times to form factice were determined at 145° to 150° C., using 5 per cent of C-16 accelerator, based on the weight of the oil.

R.K.V. = relative kinematic viscosity.

Activation of Oils 311-320. The activation process for this series of oils was carried out in exactly the same manner, except that air was blown through the oil during the activation process. An aeration device was made by bending a piece of small copper tubing into a circular shape about 4 inches in diameter, having an arm about 12 inches long extending up perpendicularly from the circle. The tubing forming the circle was drilled at intervals of about every 3/8 inch so that it distributed the air throughout the oil. The circular part of the tubing rested on the bottom of the bucket, and the arm ran upward along the side of the bucket to above the surface of the oil. A piece of rubber tubing was used to conduct the air from the compressed-air cock to the air distributor in the bucket. Blowing was started immediately after the oil was placed on the hot plate. At lower temperatures much trouble with foam was encountered. However, as the temperature increased, the surface tension of the oil decreased and foaming was no longer a problem. Samples were taken, as before, when the oil reached temperature and at regular intervals thereafter. Table I also contains the data for some of the oils obtained by this method of activation. After treatment in this manner for 150 minutes, a solid gelatin-like mass remained.

Activation of Oils 211-223. The activation process for this group of oils was carried out in a manner identical to that just described for the 311 group, except that the temperature of activation was lowered to 200° C. The oil was heated from 23° C. to 200° C. in 30 minutes, using a schedule of 30° C. increase in temperature every 5 minutes. Samples were taken when the oil reached temperature, and at definite time intervals thereafter. Table I includes the data on this group of oils.

Changes Accompanying Activation

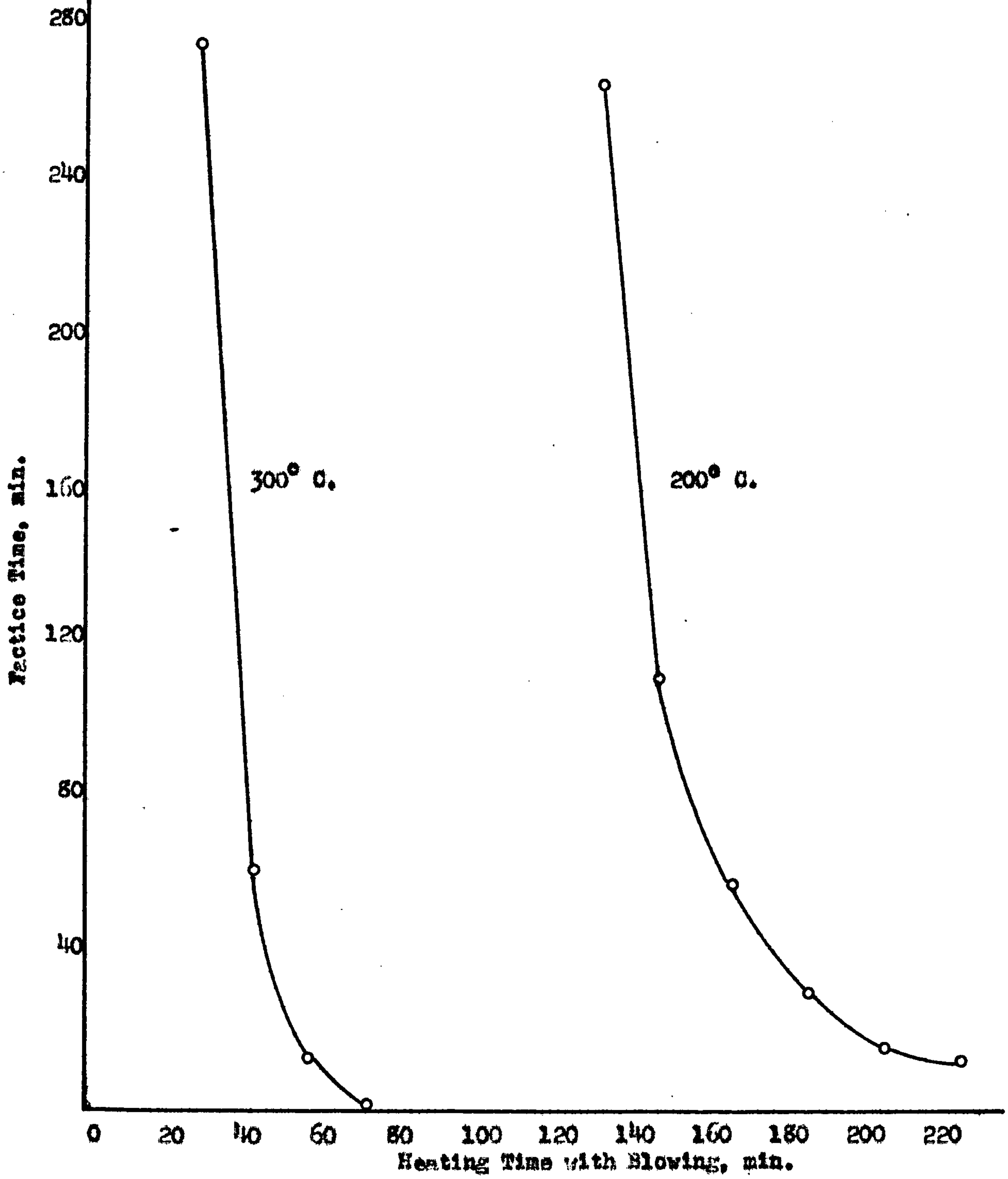
It has been stated above that numerous changes take place during the activation of an oil which might be of use in establishing a plant control method. For this reason, all samples obtained in the various activation operations were investigated as to their physical and chemical changes.

Factice Time. The true measure of the activity of an oil is, of course, the time necessary for it to form a factice when vulcanized with sulfur. Because factice time is a very definite, reproducible value, it was used to evaluate the actual effect of the various methods of activation. Factices were prepared employing the general procedure outlined at the beginning of this section. All conditions of temperature, accelerator, and sulfur content were kept constant. In the case of oils in the 211 group, factice times for 5, 10, and 15 per cent sulfur were measured. Factice times with 5 per cent sulfur were run only on the last sample of the oils in the 300 group. Although this oil is the most activated of any in the group, it required 250 minutes to form a factice. Hence, too much time would have been involved in securing data for the other oils. Whenever factice times of other oils are omitted, it is for the same reason. The time for factice formation for the oils is given in Table I.

Figure 1 shows very definitely the effect of the activation process on the activity of the oil. Both curves have a very definite break, showing that the change in activity is very rapid at first and then gradually tapers off. It was necessary to activate the oil past

FIGURE 1

THE EFFECT OF TEMPERATURE ON THE ACTIVATION OF LINSEED OIL



the breaking point of the curve, before it would possess a reasonable factice time.

Viscosity. It was evident that, during the activation process, the oil experienced a definite change in viscosity. Highly activated, very reactive oils were thick and plastic in nature, whereas the original raw linseed oil was thin and fluid like water. If heating and blowing were continued for a sufficienly long period of time, the oil would finally become entirely solid and jelly-like. This makes it evident that plastic flow, or structural viscosity, must be involved in any viscosity measurements on the treated oils. Strictly Newtonian viscosity could not be obtained.

The large range of viscosity which had to be measured, the deep color of the activated oil, and the plastic flow involved made the use of the usual standard viscometers difficult. Because the viscosity of the oil was of interest purely from a mill control viewpoint and not from the standpoint of gaining specific viscosity data, the more simple the viscometer, the better. Absolute viscosity data would not be of much significance because plastic flow was involved and not true Newtonian viscosity. For these reasons, a viscometer was made from a 25-ml. pipet; the construction and standardization of this viscometer are described in the Appendix. The pipet was filled with oil to a definite height, and the time for 10 ml. of the oil to drain from the tube was determined. The volume of the effluent was measured by allowing it to run into a 10-ml. volumetric flask. In this manner, there was a minimum error caused by the fluid clinging to the walls of the viscometer.

Using this method of viscosity measurement, the relative kinematic viscosity of each of the oils was ascertained. It proved a very quick and simple method of distinguishing the various oil samples. The variation between check runs was less than 1 per cent in every case. All viscosity measurements were made in the constant temperature room at 100° ± 0.5° F., so that the viscosity of the highly activated oils would be decreased to a certain extent. The relative kinematic viscosity of every oil sample employed in this investigation is given in Table I.

Figure 2 shows the effect of the various activation processes on the viscosity of the oil. During the initial heating periods there were very slight changes in viscosity but, when the change did occur, it was very rapid. The most rapid increase in viscosity took place in the activation at 300° C. with blowing. In this case the values rose very rapidly from 101 to 1350 seconds with an additional treatment of only 30 minutes. The change in viscosity of an oil merely heated to 300° C. took place much more slowly, but there is still an abrupt breaking point in the curve. The activation at 200° C. with blowing required the longest time to reach a given viscosity, and the change was much more gradual. This would seem to indicate better control at this activation temperature.

It will be seen that the viscosity curves of Figure 2 are the exact opposites of the time-to-factice curves of Figure 1, and that they appear to have some correlation with the activity of the oil.

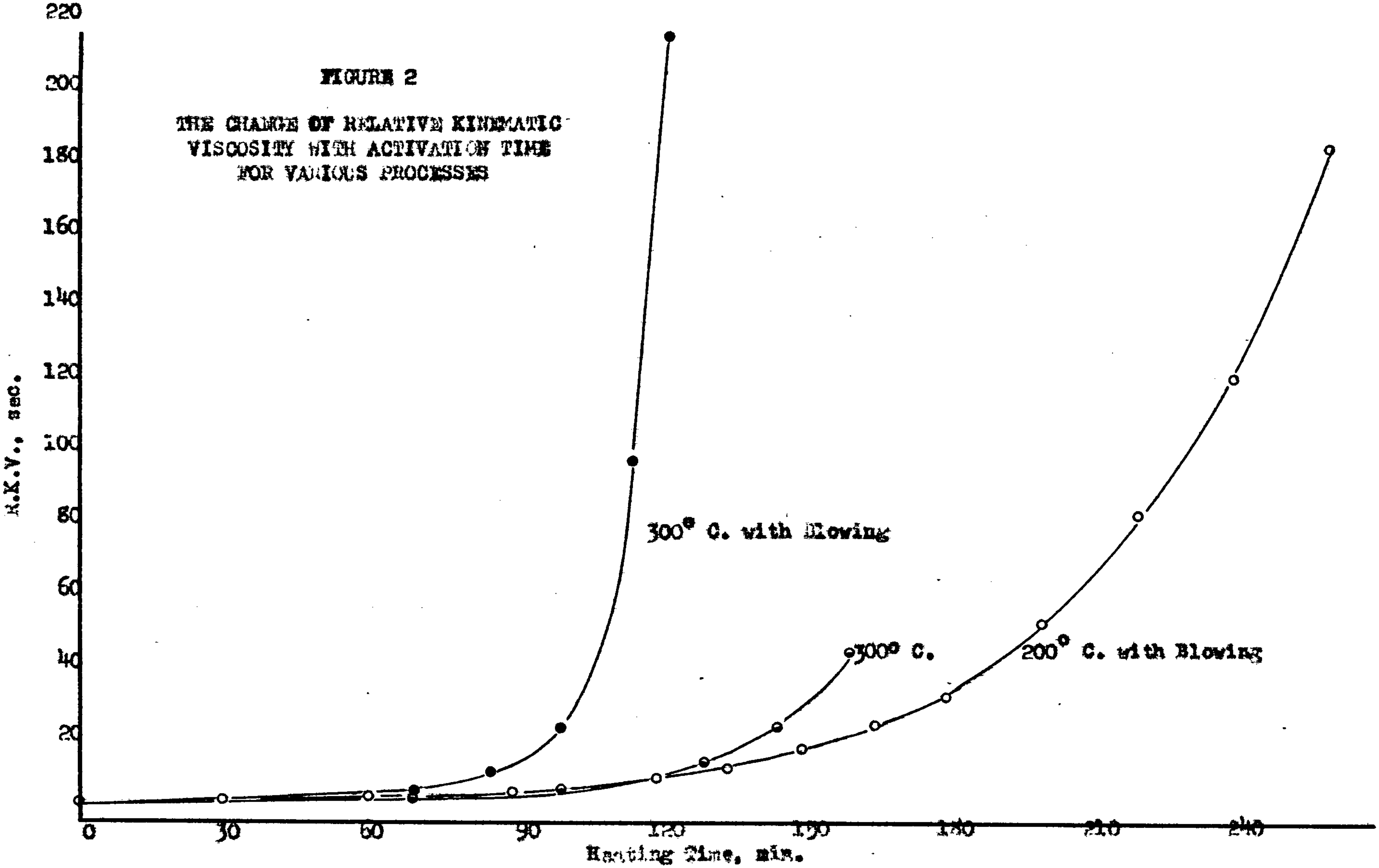


FIGURE 2

THE CHANGE OF RELATIVE KINEMATIC VISCOSITY WITH ACTIVATION TIME FOR VARIOUS PROCESSES

Index of Refraction. It was known from previous work that oils experience a change in index of refraction upon prolonged heating. Such a test is common in the varnish industry and in the testing of drying oils. It seemed desirable to measure the index of refraction of the various activated oil samples. This was accomplished by the use of an Abbé refractometer with a sodium flame as the light source. Water at 100° F. was circulated from a constant temperature bath through the Abbé refractometer, in order to obtain the refractive indices at the same temperature as the viscosities.

Table I contains the refractive indices of all the oils used in this experimental work. These values are shown graphically in Figure 3, in which they are plotted against the time of activation. Again, the curves have the same general shape of those found in Figure 2 (viscosity-heating time). Activation at 300° C. with blowing caused the greatest change in the refractive index of the oil. The increase resulting from heating at 300° C. and from heating at 200° C. with blowing was very nearly the same. There are several very definite breaks in the curve for the oil activated at 200° C. with aeration. Whether these breaks were the result of some outside source, or whether they are representative of the true change is not known. Checks on the measurements of the refractive indices of these oils gave results identical with those obtained the first time, so the error was not in the measurement. Some change in the activation process might have occurred and caused the variation. In the other activation processes, the change in index of refraction might have taken place so rapidly that this fluctuation was not noticed. It might occur only at the lower temperatures.

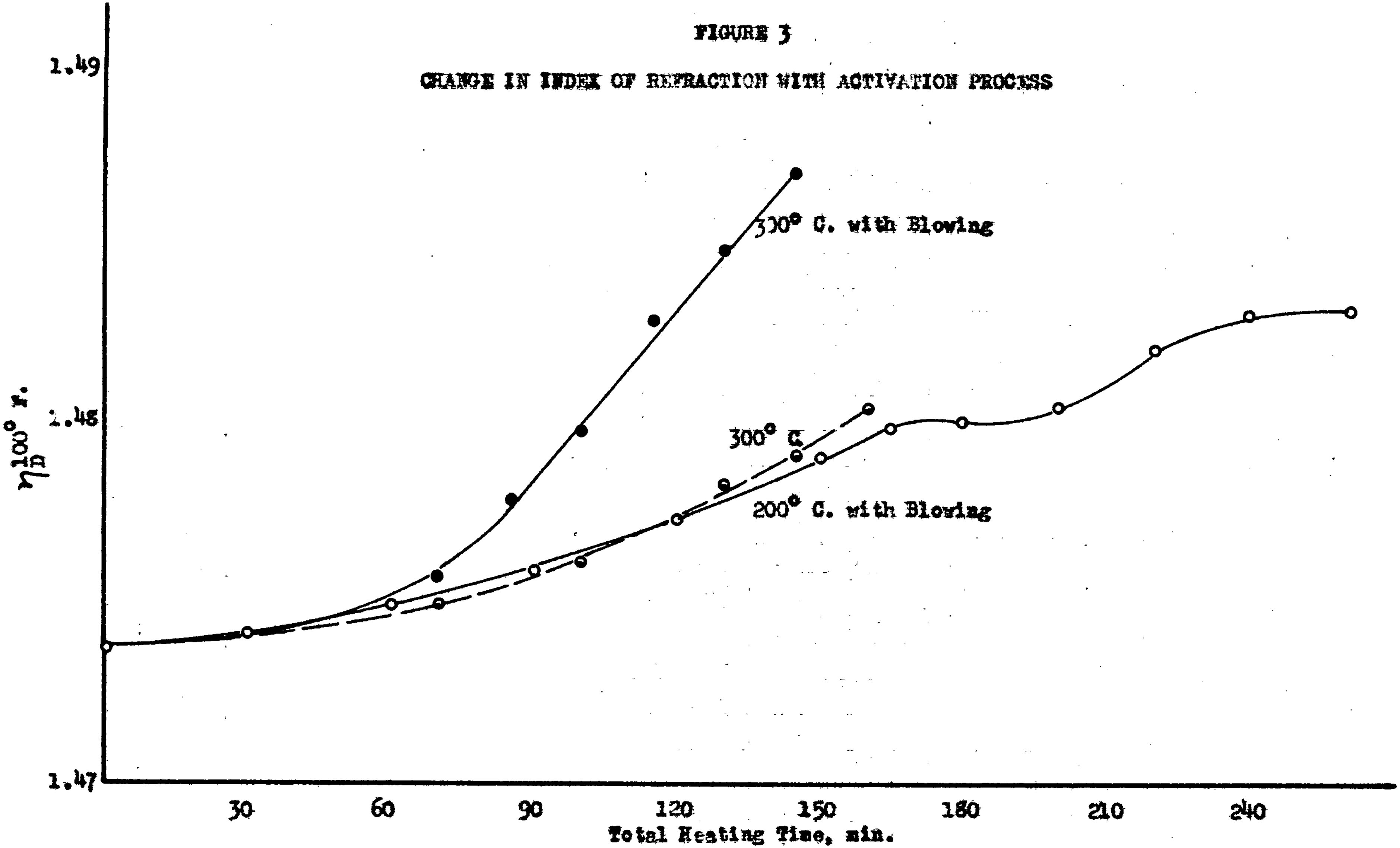


FIGURE 3

CHANGE IN INDEX OF REFRACTION WITH ACTIVATION PROCESS

In general, the curves found in Figure 3 indicate the possibility of following the activation process by this method.

Color of Oil. The activation processes of all types are accompanied by very definite color changes. Raw linseed oil has a very light red-yellow color. If activation was caused by heating at a high temperature (350° C.), there was a gradual color change until the final product was the dark olive-green color common to heavy lubricating oils. Oil activated by heating to 300° C. for prolonged periods assumed a deep red color, both with reflected and with transmitted light. Aeration caused two distinct color transitions to take place. During the first part of the heating the color of the oil became a bright grass green; as the heating and aeration were continued, the green slowly changed into the deep red color obtained by merely heating the oil at 300° C.

It would have been interesting to study the activation taking place by measuring the absorption and transmission of visual and infrared radiation by the various samples. Adequate time was not available for this study, because other investigations were deemed more important.

Loss of Volatile Materials. The entire activation process was accompanied by the evolution of the more volatile constituents of the linseed oil. As would be expected, the higher the temperature, the greater was the loss in volatile material, even though the activation took place for a shorter period of time. If the oil was heat-treated at a temperature of 300° to 350° C., about 8 to 10 per cent of the original weight of the oil was lost. Aeration did not seem to cause much variation in this value. Activation at lower temperatures resulted in a smaller loss of volatile material. At a temperature of 200° C., the loss was in the range of 3 to 5 per cent of the original weight of the oil.

Other Changes. Probably the greatest change in the oil was in its chemical structure. Iodine number, acid number, and the other usual chemical tests for the identification of such materials might have led to some interesting results. Because the time was so limited and the investigation was of a practical nature concerned more with plant control methods than with the actual chemistry involved, it was decided not to investigate the actual chemical changes taking place. Such a study would be a major research problem in itself.

Effect of Variables of Activation

Temperature. It appeared to be relatively unimportant whether the original linseed oil had been activated by heating at a high temperature (350° C.) or at a lower temperature (300° C.) for a longer period of time. If the activation in either case was carried out until the oils reached the same reactivity, the factices prepared from the oils could not be differentiated on the basis of physical properties. It seemed evident that, on the basis of the final factice, the temperature of activation was of no importance.

The temperature, however, was of great importance in the speed of the activation process, as is shown by the curves in Figure 1. Activation at 300° C. takes place in less than half the time required at 200° C. Figures 2 and 3 show the great influence of activation temperature on the rate of change in viscosity and refractive index. All these curves indicate very definitely that, at high temperatures, the speed of activation occurs so rapidly that it would be difficult to control.

Time. The time of activation has been shown to be a function of temperature. If activation is carried out at lower temperatures, longer periods of treatment are required. The time of activation can be shortened considerably by aeration during treatment, as will be discussed in the following section. It is evident that the important heating interval is the time the oil is held at the activation temperature. The time required to bring the oil up to temperature is of lesser importance.

Blowing. The blowing of air through the linseed oil during the activation process was a great aid in accelerating the speed of the reaction. In addition to oxidizing the oil, such a procedure also increased the reactivity with sulfur. The values given in Table I show the great improvement secured by aeration. Oil 307 was heated for 160 minutes, and yet required 250 minutes to vulcanize (using 5 per cent of both sulfur and accelerator). Oil 313 was treated for only 100 minutes with blowing but formed a factice in 260 minutes. Additional activation by this method for 45 minutes produced an oil which would factice in 1 minute. Figures 2 and 3 also show the rapid change in viscosity and index of refraction caused by blowing the heated oil. From Table I it can be seen that Oil 217 (heated at 200° C. with blowing for 165 minutes) formed a factice in 265 minutes. Hence, the blowing of the oil during activation made it possible to lower the activation temperature from 300° C. to 200° C. without lengthening the time of treatment. This is of great importance for mill operation, because this 100° C. decrease in temperature would mean a considerable saving in equipment and operation costs. Furthermore, the factices prepared from blown oils performed just as well in laminating operations.

It was thought that the effect of aeration might be improved still further if ozonized air was passed through the oil in place of air. A small ozone apparatus (21) was available, and several runs were made bubbling ozonized air through the oil being activated. Even in relatively large quantities, ozone had less effect upon the activation of the oil than air. Perhaps this was because ozone did not oxidize the oil but added to the double bonds, forming an ozonide which would be decomposed into an aldehyde and an acid upon hydrolysis with water. In this manner, a degradation of the chains would be experienced and not a shifting of the double bonds to conjugate double bonds.

Method of Plant Control of Activation

It was evident from the data presented in the preceding pages that a very definite relationship existed between viscosity, index of refraction, and the activity of the oil, provided the method of activation is defined. Unfortunately, viscosity and index of refraction are not altogether independent of the method of activation. Hence, one must know the past history of the oil, as well as its physical constants. In plant control methods, this fact would not cause any difficulty because the method of activation could be thoroughly defined by time and temperature schedules.

For any given activation process, the activity of an oil can be determined very definitely by the index of refraction and viscosity. Oils B and D (Table I) were activated independently before this work on activation was carried out. The temperature of activation was the same in each case. About three times the volume of oil was activated in the latter case, so that a longer time was necessary to reach temperature. The refractive index, viscosity, and factice time of these two oils are almost identical. This certainly indicates the relationship between the three properties mentioned.

Because the method of activation used on the oils in the 311-322 group would be the best commercially, a more thorough study of the relationship between the activity of the oil and its physical properties was desirable. These results are given in Table I and are represented graphically in Figures 4 and 5. Figure 4 illustrates the relationship between the relative kinematic viscosity of an oil and its factice time, using either 5, 10, or 15 per cent of sulfur in the vulcanization process. Figure 5 shows the change in refractive index with factice time, employing similar sulfur contents in vulcanizing. Both these curves indicate a definite relationship, the former probably being the more satisfactory. On the basis of this evidence, it is not unreasonable to assume that quick measurements of viscosity and index of refraction can be used to follow the activation process, thus enabling the operator to obtain any desired degree of activation. Of the two methods, the viscosity measurement is preferred, because costly equipment is not necessary. Further, at lower activation temperatures, although the change in refractive index is definite, it is so small that any error in measurement would lead to

FIGURE 4

THE RELATIONSHIP BETWEEN RELATIVE KINEMATIC VISCOSITY AND FACTICE TIME WITH VARIOUS SULFUR CONTENTS

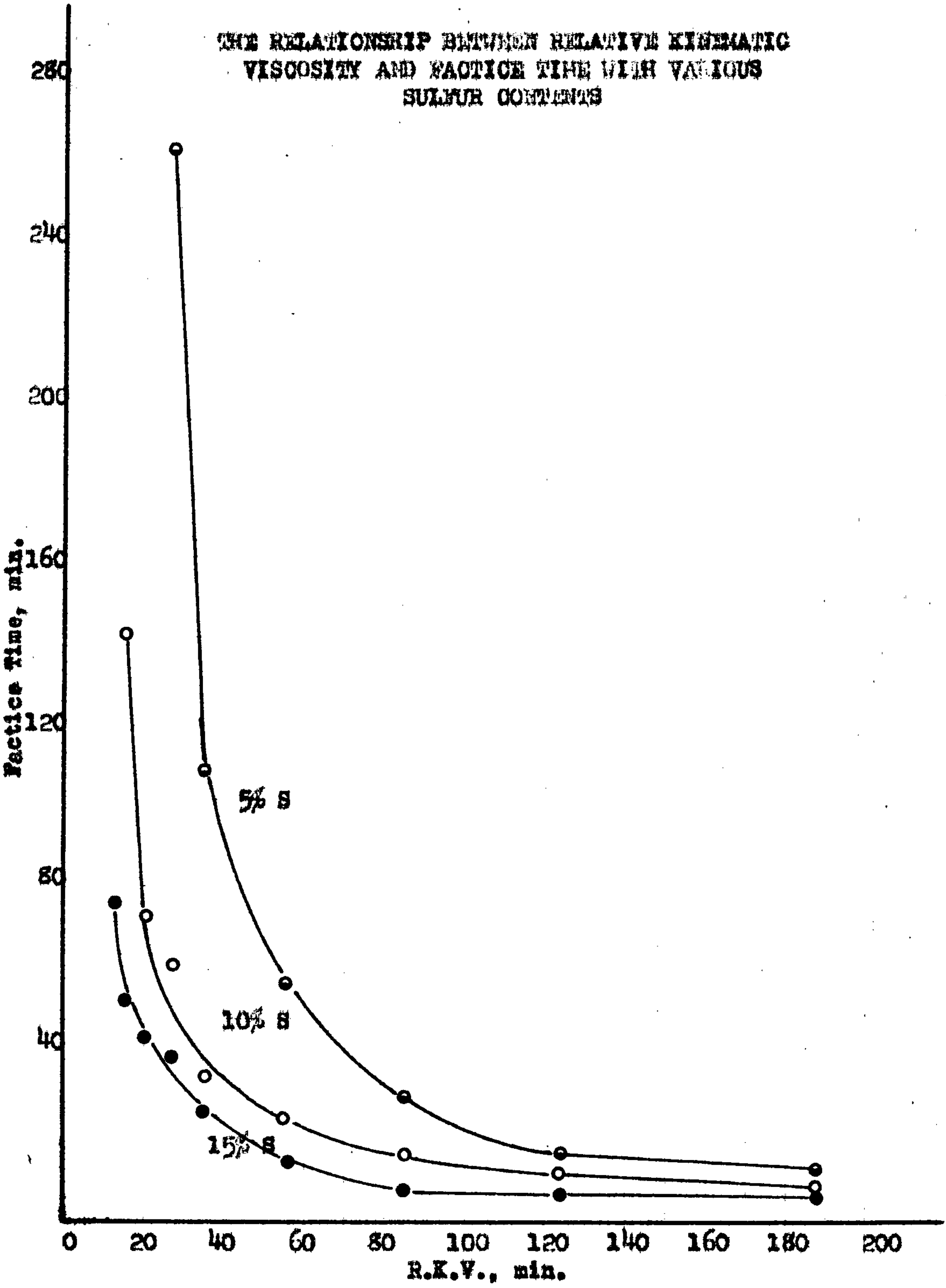
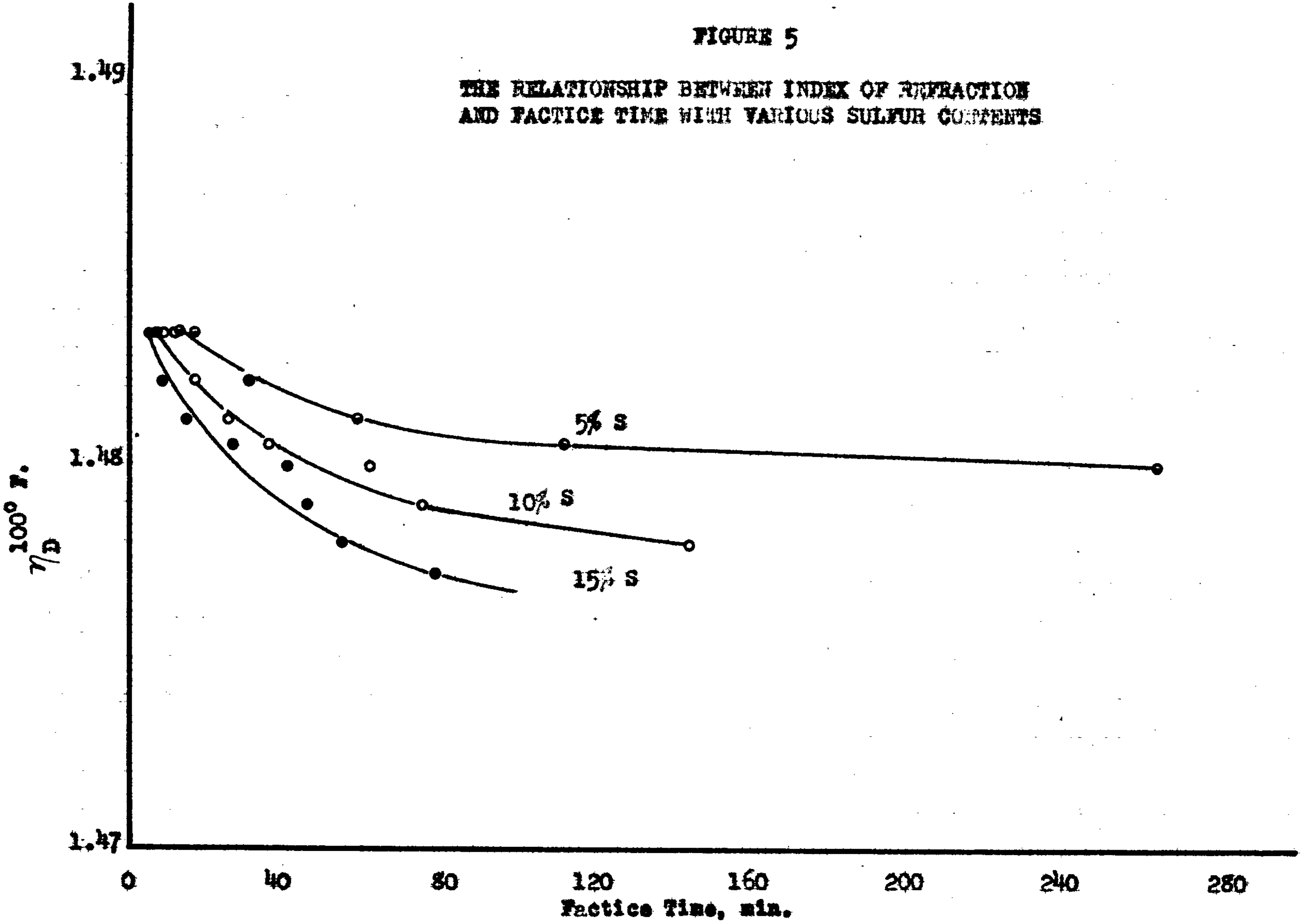


FIGURE 5

THE RELATIONSHIP BETWEEN INDEX OF REFRACTION
AND FACTICE TIME WITH VARIOUS SULFUR CONTENTS



difficulties. Viscosity changes, on the other hand, are of greater magnitudes and the chance for error in measurement is less.

A STUDY OF THE VARIABLES OF FACTICE FORMATION

Activity of the Oil

The previous pages have been devoted to the activation and activity of linseed oil, but little has been said about the effect of activity on the final characteristics of the factice. It is evident that increased activation of the oil caused a decrease in the time necessary for the final vulcanization process. In general, for a given temperature and a definite sulfur and catalyst ratio, the time of factice formation depends upon the activity of the oil. The increased reactivity of the oil with activation is shown very definitely in Figures 1 and 6.

In addition to the speed of the reaction, the activity of the oil used for vulcanization has a definite influence upon the final properties of the factice. Factices prepared from the more highly activated oils have more body, more of the crumbly texture of purely oxidized linseed oil, and much less tackiness and elasticity. They were more flexible and softer, but lacked the strength or resiliency of rubber. This was characteristic of oils which would factice in 14 minutes or less, using 5 per cent of both sulfur and accelerator. These products, had a greater tendency for "blooming" of the sulfur after standing for several days.

Factices made from the lower activated oils depended considerably on the percentage of sulfur, whereas those prepared from highly activated oils appeared to be independent of the sulfur content. This will be discussed more completely under sulfur content. The factices from less activated oils were much more fluid, tacky, sticky, and resilient, and possessed much less body. In general, they proved much better for laminating purposes. There was no tendency toward sulfur "blooming," and the products were less influenced by extremely low temperatures. Oils in the range of activity which would form a factice in 20 to 60 minutes with 5 per cent of both sulfur and C-16 were considered the most desirable for this work.

Insufficiently activated oils required a long time to polymerize and had several objectional features. They were soft and oily at room temperature and possessed very little strength for laminating purposes. They contained unvulcanized oil which, upon aging, would impregnate the laminated sheet, giving it an oily, undesirable appearance. Such factices also have a slight odor.

Factices prepared from highly activated oils are generally a bright red or orange color; this color becomes a dull brown as the activity of the oil used in factice preparation decreases.

Accelerators

Certain commercial rubber vulcanizing accelerators were found to speed up the vulcanization of activated linseed oils. Most of the low temperature, ultra-accelerators for latex are in this class. For this investigation, seven accelerators were available:

Trade Name	Chemical Name	Manufacturer
Butyl zimate	Zinc dibutyldithiocarbamate	Vanderbilt
Captax	Mercaptobenzothiazole	Vanderbilt
du Pont 552	Piperidinium pentamethylenedithiocarbamate	du Pont
El sixty	(An amino thiazole powder)	Monsanto
Pip-Pip		Monsanto
Thionex	Tetramethylthiuram monosulfide	du Pont
Tuads	Tetramethylthiuram disulfide	Vanderbilt

Rowley (20) had previously investigated the addition of 1 per cent of the above mentioned catalysts and found Pip-Pip, du Pont 552 and Butyl zimate to be the most effective. Although it was decided to used Butyl zimate as the accelerator for the vulcanization process, the available material was depleted early in the investigation and a commercial vulcanizing agent manufactured by the Vanderbilt Company, known as C-16, was substituted. The composition of this agent is as follows:

Material		Parts
Zinc oxide		3.00
Sulfur		1.00
Butyl zimate		1.00
Agerite white		1.00
Darvan		0.24
Casein		0.30
Caustic soda		0.10
Water		5.36
	Total	12.00
Total solids		55.3%

Because Butyl zimate is a component of C-16, the latter might prove usable as an accelerator. A series of tests was made to compare the effectiveness of varying amounts of C-16 as a catalyst. The results of this investigation are given in Table II, using the following constant conditions:

30 grams of linseed oil C ($\underline{n}_D^{37.5}$ 1.4854, viscosity 324)

1.5 grams of sulfur

Temperature, 145° to 150° C.

TABLE II

THE EFFECT OF ACCELERATOR ON RATE OF VULCANIZATION

Run	Factice Time min.	Accelerator g.	Accelerator	Accelerator %*
11	65	0.3	Butyl zimate	1
12	30	6.5	C-16	21.7
13	25	3.0	C-16	10
14	20	1.5	C-16	5
18	20	1.5	C-16	5
15	30	1.0	C-16	3.3

* Percentage of accelerator based on the weight of the oil.

The above results show that C-16 is a much more efficient catalyst than Butyl zimate alone. The effect must be produced by some other component of C-16 than Butyl zimate, because the quantity of C-16 necessary to contain 0.3 gram of Butyl zimate is 0.3 x 12, or 3.6 grams. This was more accelerator than was required to give the best results. Five per cent of C-16, based on the weight of the oil, produced the most effective catalytic result. This value was adopted as a standard for the remaining phases of the investigation.

The higher amounts of accelerator produced a definite change in the physical properties of the factice. With increased quantities of C-16, the finished product assumed a more rubber-like appearance. It was firm and elastic and had more body. There was a loss in the tacky, sticky, stringy appearance of factice prepared with lower amounts of accelerator. A part of this change might have been caused by the zinc oxide in the C-16.

Because C-16 is a water emulsion, a special method of factice preparation had to be developed. This has been described on page 8.

Sulfur Content

For a given oil activity, catalyst, and temperature, the time of factice formation depends upon the ratio of sulfur to oil. In general, the larger the amount of sulfur, the shorter is the time for factice formation. The data for factice formation given in Table I are evidence of this fact. A portion of these data is shown graphically in Figure 6. It is seen that the ratio of sulfur used in vulcanization is of much greater importance with the less activated oils. Increasing the sulfur ratio in a highly activated oil produces relatively small changes in factice time; in less activated oils, it is of great importance. These curves indicate that, if sufficient sulfur is present for the reaction, the addition of more sulfur has little effect. Evidently only a certain ratio of sulfur to oil is required for the vulcanization, this ratio increasing with decreasing oil activity. Any additional sulfur does not react and will "bloom" out upon standing. This proved to be true in the experimental work. Highly activated oils showed some "blooming" when vulcanized with 5 per cent sulfur, and much more if higher percentages were used. On the other hand, the lower activated oils showed no "blooming" with 15 per cent sulfur. The highly activated oils are subjected to some polymerization during treatment. This must be true, because they become solid if the heat-treatment is continued long enough. In such cases, the sulfur simply completes the polymerization and need be present only in relatively small amounts.

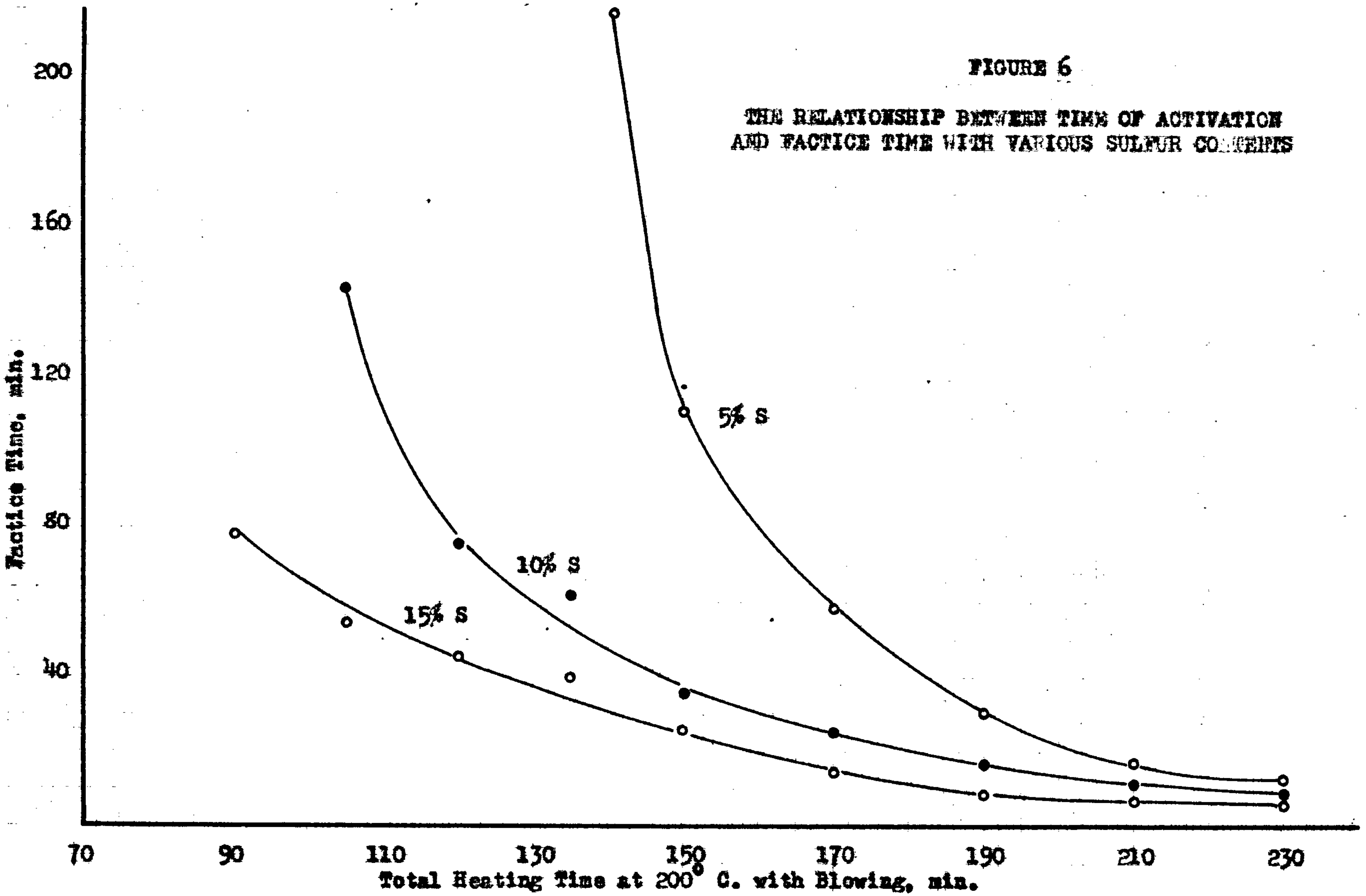


FIGURE 6

THE RELATIONSHIP BETWEEN TIME OF ACTIVATION AND FACTICE TIME WITH VARIOUS SULFUR CONTENTS

The quantity of sulfur used in vulcanization changes not only the factice time but also the nature of the finished product. As the sulfur content increases, the factice changes from a tacky, sticky, semifluid mass to a firmer, less tacky, rubber-like mass. In the latter case, the material has more of a crumbly character and loses its elasticity and strength.

Too high a sulfur content will tend to produce an odor of sulfur in the finished product. The aging properties of the material are decreased, particularly at higher temperatures.

Temperature

For a given oil activity and sulfur and catalyst ratio, the time of factice formation depends upon the temperature. Sulfur (mu) is supposed to be more reactive than sulfur (lambda) and, because there is a shift in the equilibrium between the two forms of sulfur in favor of sulfur (mu) with increasing temperatures, factice might be formed more readily at higher temperatures (20).

In general, it was found that a temperature of 145° to 150° C. could readily be obtained and controlled; therefore, this temperature was employed. The reactions took place in reasonable periods of time, and there was less danger of overheating and burning the material as it began to form a factice. Burning or localized overheating imparted an odor to the finished product. The sulfur dissolved readily but not too quickly at this temperature. At temperatures above 200° C., the addition of the sulfur caused the evolution of large quantities of gas (oxides of sulfur) which gave trouble.

Oil B, which took 60 minutes to form a factice at 145° C., required only 10 minutes at 180° C. There was apparently little change in the physical properties of the two factices. The latter may have been less tacky. No detailed study was made of this variable.

Seeding

Many polymerization reactions proceed much more rapidly if the starting materials are seeded with a small quantity of the finished product. In this manner a lattice structure may be formed, upon which further building or polymerization can take place. Seeding appeared to have a noticeable effect in accelerating the formation of a factice.

Oil 220 was used to prepare a factice in the customary manner, employing 5 per cent each of sulfur and accelerator. The factice time for this oil was 31 minutes. A second and identical batch of Oil 220 was started, but in this experiment about 10 per cent of the previously formed factice was used in addition to the sulfur and accelerator. The previously formed factice dissolved or dispersed quickly in the hot oil. The factice time in this case was 26 minutes. This was a reduction in time of about 15 per cent. Oil 221 showed a similar reduction in time for factice formation when seeded with previously prepared factice.

Time was not available for a complete study of the effect of seeding over a wide range of oil activities, but from the available evidence it is a phenomenon worthy of investigation.

PROPERTIES OF FACTICE FILMS

Sheets of kraft paper were laminated as described on page 10. These laminated sheets were tested in a variety of ways in an attempt to estimate the value of factice as a laminate.

Flexibility

One of the most desirable characteristics of factice films is their great flexibility in all the temperature ranges studied. Factice seems to be a material which possesses practically no thermoplastic tendencies. The tackiness, flexibility, and continuity of films formed in such a manner seem to be independent of temperature, whether it is 140° C. or -40° C. Samples of pure factice and factice-laminated sheets placed in a cold box at a temperature of -35° C. possessed the same soft, resilient texture evidenced at room temperature. During the laminating process, the factice material was applied at a temperature of 145° C., yet there was no trouble from bleeding. This one property alone indicates a very bright future for factice as a laminating material. Flexibility over such a wide temperature range cannot be obtained with any of the common laminating materials.

The influence of sulfur, oil activity, accelerator, and other such variables on the general physical character of factice has been discussed in detail. It is evident that the ratio of these materials necessary for the production of a factice suitable for lamination must be chosen with regard to the properties of the finished product. High sulfur content or oil activity tend to produce a more firm, crumbly type factice possessing less flexibility. The proper range of these constituents necessary for a desirable product has been indicated in earlier sections.

Aging

Factice films were unchanged by long periods of aging under most temperature conditions. At higher temperatures for long periods of time, the factice became slightly stiffer. This was especially true of factices made from highly activated oil (less than 15-minute factice time), or those having a high sulfur content. Factices prepared from moderately activated oils (20- to 60-minute factice time) and 5 per cent of sulfur changed very little with aging. Less activated oils formed factices which contained unvulcanized oil; upon aging, this oil penetrated into the sheet, giving it a dark, oily, undesirable appearance.

Grease Resistance

Greaseproofness tests according to the Institute turpentine test described in the Appendix proved that creased or uncreased factice films were very good. Not one failure or spot was obtained in the 60 minutes usually allotted the test. In the majority of cases, there was no failure even after 48 hours. The resistance of factice films to vegetable and mineral oils was investigated. Small boxes were made from the factice-laminated sheets, a thin coat of corn syrup was applied around the top of the box to keep the oil from creeping over, and the boxes were filled with mineral, lard, and peanut oil. After several days there seemed to be no evidence that any of the boxes had failed.

It was concluded from these tests that factice possessed very good greaseproof properties.

Water Resistance

Factice-laminated sheets possessed very good resistance to liquid water. Small boxes prepared from the laminated sheets would hold water indefinitely. Folding or creasing the sheet seemed to have no influence on the results. It was found that the best method for testing samples for water resistance was to add a small quantity of a wetting agent (such as Vel) to the water. The presence of the wetting agent would increase the speed of penetration of the water through any discontinuities in the film. Using this method, pinholes or failures would be evident in less than 1 minute.

Water-Vapor Resistance

Resistance to liquid and vaporous water are two separate problems. Good resistance to the former does not mean satisfactory protection against the latter. Factice films cannot be considered as good barriers to water vapor. They are, of course, a marked improvement over the paper alone, but they gave values considerably above a water-vapor permeability of 1 gram of vapor per 24 hours per 100 square inches of area, the upper limit for moistureproof barriers. Samples for water-vapor permeability were creased, and the creased and uncreased samples were tested for water-vapor permeability using the method given in Instrumentation Report 30, Part III (22). The results of these tests are shown in Table III.

TABLE III

WATER-VAPOR PERMEABILITY OF VARIOUS FACTICE FILMS

Run	Oil	Factice Time sec.	C-16 %	Sulfur %	Film Weight g./100 sq.in.	Water-Vapor Permeability Uncreased g./(24 hr./100 sq.in.)	Creased
16	C	20	5	5	12.8	7.90	
17	C	20	5	5	13.6	5.99	
18	C	20	5	5	13.6	4.18	4.26
20	C	29	21.7	5	22.0	2.61	2.71
43	D	60	5	5	11.2	3.08	3.44
205	Conjulin	23	5	5	8.1	7.55	8.13

It is evident from these data that factice films have poor resistance to water vapor. The method employed in lamination gave little or no control over the variables of this process, as will be discussed later. The total weight of material used in lamination could be determined readily, but film thickness and penetration could not be controlled. However, the results obtained were so poor that it was evident that some means must be adopted to improve the water-vapor permeability of the factice film.

The physical characteristics of the factice had some influence on the water-vapor permeability of the laminated sheet, particularly on its folding qualities. This was to be expected. Much of the difference in water-vapor permeability might be attributed to the difference in penetration of the sheet during lamination. From Table III, it is seen that there is a steady increase in the permeability of Samples 20, 43, and 205. The physical properties of the factices changed in the same order, Sample 20 being rubber-like whereas 205 was a semifluid. The change might be attributed also to the difference in film weight rather than to the factice. In either case, it is apparent that factice is unsatisfactory for water-vapor protection.

SUMMARY

A rapid and satisfactory method for the preparation of a factice suitable for laminating purposes has been developed and all the pertinent variables important in the production and control of the factice have been investigated.

The activation of linseed oil can be accomplished by heat-treatment at 350° C. or at 300° C. for a longer period of time. Aeration permits the lowering of this temperature to 200° C. without an increase in activation time, and gives the same satisfactory results. The lower temperature causes the activation of the oil at a much more controllable rate and is the most feasible commercially. Viscosity, index of refraction, and factice times for small samples are directly related to the activity of the oil and can be used to follow and control the activation process in industry. Knowing the index of refraction, viscosity, and method of activation of an oil, it is possible to predict accurately the time required for factice formation, the optimum sulfur content needed for vulcanization, and the character of the factice produced.

The time of formation and physical properties of a factice depend upon the following variables:

Oil Activity. For a given temperature and sulfur and accelerator ratio, the time of factice formation depends upon the activity of the oil. More highly activated oils produce rubber-like materials having body and flexibility, but lacking the tackiness, toughness, and semi-fluid character of factice from less activated oils.

Accelerator. For a given temperature, oil activity, and sulfur ratio, the time of factice formation depends upon the type and quantity of accelerator added. Optimum conditions of vulcanization with C-16 (Vanderbilt) are obtained with 5 per cent of the accelerator (based on the weight of the oil). The physical properties of the factice are also dependent upon the type and quantity of accelerator.

Sulfur Content. For a given temperature, oil activity, and accelerator content, the time of factice formation depends upon the sulfur to oil ratio. This ratio is of greatest importance with the less activated oils, but is of much less importance with highly activated ones. A definite quantity of sulfur is necessary for the polymerization of each oil, but an excess of sulfur does not react and will "bloom" out upon standing. Increased sulfur content produces more body but less tackiness, strength, resiliency, and flexibility in the final factice.

Temperature. For a given oil activity and sulfur and accelerator ratio, the time of factice formation depends upon the temperature of vulcanization.

Seeding. The addition of previously formed factice to an oil during vulcanization causes an acceleration of the vulcanizing process.

The properties of a factice film which make it desirable for laminating purposes are as follows: (1) The soft, tacky, rubbery film keeps its properties independent of extremely low (-35° C.) or high (150° C.) temperatures. Folding or creasing does not cause fracture of the film. (2) Factice-laminated sheets possess good aging properties, irrespective of temperature. At high temperatures there may be a slight stiffening of the factice. (3) Factice-laminated sheets are greaseproof to mineral, lard, and vegetable oils as well as to turpentine. (4) Sheets laminated with factice are water resistant. (5) Properly prepared factice has little odor. (6) Factice can be prepared easily from relatively cheap raw materials, with very low cost equipment.

The undesirable properties of factice for use in laminating are as follows: (1) Commercial application might present difficulties because of the tacky, sticky, and nonthermoplastic character of the material. (2) The cost and availability of linseed oil is limited at present as a result of war conditions. (3) Factice-laminated sheets do not possess good resistance to the passage of water vapor.

PART II

A STUDY OF THE EFFECT OF WAXY AND RESINOUS MATERIALS ON THE WATER-VAPOR PERMEABILITY OF FACTICE FILMS

It was apparent from the results presented in Part I that factice films were unsuitable for the production of laminated papers which would fulfill the requirements of the packaging industry. Although the greaseproofness of such materials was good, they were not resistant to the passage of water vapor. Unfortunately, water vapor can be just as destructive to packaged food or materials as water itself; it will cause deterioration of foods and rusting of equipment. For these reasons, it was obvious that good protection against water vapor was an essential property of a laminating material such as was being investigated. These facts indicated that some method must be devised to improve greatly the water-vapor resistance of the factice films.

Pure factice for laminating purposes had another definite drawback—that of supply of raw material. Under the prevailing war conditions the supply of linseed oil, like all other materials, is limited, although it is not rationed or on priority at the present time. Therefore, an investigation was carried out with raw linseed oil as the starting raw material. Even though it is not one of the edible oils so essential under present conditions, the supply of oil is limited and might not be sufficient to fulfill the requirements of the industry. The blending of factice with cheaper, more available materials might prove to be the answer to this problem.

The most logical approach to the solution of both the difficulties just presented was to study the changes caused by the addition of numerous water-resistant waxes and resins to the factice. Some resin might be found which would bring about a great improvement in the water-vapor-resistant material. At the same time, such a "filler" would tend to lower the cost of the factice product and relieve the problem of linseed oil supply. A large number of different types of waxes and resins were added to the factice. At first only small quantities of these materials were employed; however, as the investigation progressed, it seemed desirable to make the "filler" the predominant portion of the product and use the factice more as a plasticizer. In this manner the flexible, rubbery character of the factice was combined with the water-vapor resistance of the "filler."

GENERAL METHOD OF PREPARATION

The first step was to find a method for adding the various resin materials to the factice. Although a chemical combination might not be necessary, a homogeneous mixture was essential. If the factice was prepared first and molten waxes or resins added, a homogeneous mixture could not be obtained. It was evident that, once the polymerization or vulcanization of the oil had taken place, it was immiscible with other materials. It was soon learned, however, that hot linseed oil, prior to vulcanization, was miscible in all proportions with many resins and waxes. On this basis, the following general method of preparation was adopted as standard.

Thirty grams of previously activated oil were weighed into a 100-ml. beaker containing 1.5 grams of the C-16 accelerator. The oil and the C-16 water emulsion were immediately mixed together, until a homogeneous emulsion was formed. If this mixing was not done immediately, there was danger of the accelerator caking on the bottom of the beaker, where it promptly burned when heat was applied. Under such conditions, it would not dissolve in the hot oil. The water and oil emulsion was then heated quickly over a Bunsen flame to 100° C. At this point the water began to boil out, and care had to be taken to prevent oil from foaming over the top of the beaker. After all the water had been boiled out, the temperature of the oil was increased to 145° C. At the same time, the previously weighed portion of resin or wax was added. Heating was continued (with constant stirring) until all the resin had melted and was completely mixed with the hot oil. This preliminary treatment was completed in 2 minutes.

The beaker was then placed on an electrically heated and controlled hot plate, where the temperature was held constant at 145° to 150° C. The mixture was agitated with a constant speed stirrer to insure mixing and to avoid localized overheating. After the stirrer had been started, the desired amount of sulfur (1.5 or 3.0 grams) was added and stirring continued until factice formation took place. It was found that, with the higher ratios of resin to oil, an increase in the quantity of sulfur from 5 to 10 per cent (based on the weight of the oil) decreased the time of factice formation appreciably. The end point in this investigation was the same as that previously described.

After the material had been vulcanized, sheets of kraft paper were laminated as before, using a wringer. This method of lamination made it difficult to control the film weight and penetration, but sheets were obtained which were suitable for testing. As the ratio of wax or resin was increased, the factice became more thermoplastic and, as a result, the weight of the film between the sheets tended to increase.

Sheets laminated in this manner were tested for water-vapor permeability by the usual method (22). The results of these tests are found in Tables IV and V. In one or two cases, the value for the water-vapor permeability of the uncreased sheet is slightly higher than that of the creased sheet. This may have been caused by a difference in the weight of the factice film in the samples, or the best portion of every laminated sheet may have been selected for creasing.

DISCUSSION OF RESULTS

In the following discussion, the percentage of filler added was based on the weight of oil used. For the sake of simplicity and to save repetition, the abbreviation W.V.P. is used to indicate water-vapor permeability and the units of water-vapor permeability are not repeated. When it is stated that a sample has a W.V.P. of 2.5 grams, it is to be understood that 2.5 grams of water vapor will pass through 100 square inches of the sheet in a 24-hour period, using the well-defined testing conditions.

Piccolyte S-40

Piccolyte resins are a group of special formaldehyde-treated natural resins. Piccolyte S-40 was a very fluid liquid, possessing a definite gum or pine smell. The addition of this resin, even in large quantities, did not produce a marked improvement in W.V.P. It is seen

TABLE IV

THE EFFECT OF RESINS AND WAXES ON THE WATER-VAPOR PERMEABILITY OF FACTICE FILMS

Run	Factice Time min.	Resin Added Type	%	Film Weight g./100 sq.in.	Water-Vapor Permeability g./(24 hr./100 sq.in.)	
					Uncreased	Creased
17	20	None		13.6	4.18	4.26
19	50	Piccolyte S-40	10	11.4	3.49	4.53
21	75	Rosin	10	14.0	2.75	3.07
22	50	Asphalt	10	13.6	3.27	
23	55	Piccolyte S-L	10	11.4	4.88	5.12
24	60	Falkyd B-7	10	12.4	4.03	5.04
26	55	Rosin-beeswax	10	8.4	1.74	1.81
25	50	Asphalt	20	10.2	2.26	2.46
27	75	Asphalt	50	17.4	1.00	1.81
28	135	Rosin-beeswax	50	10.4	0.85	1.34
29	215	Piccolyte S-40	50	13.0	2.31	1.99
32	110	Falkyd B-7	50	15.0	4.08	3.80

Constant Conditions:

30 grams of linseed oil C ($n_D^{37.5}$ 1.4854, viscosity 324)
1.5 grams of sulfur
1.5 grams of C-16

Percentage of resin based on the weight of the oil

Temperature, 145° to 150° C.

TABLE V

THE EFFECT OF RESINS AND WAXES ON THE WATER-VAPOR PERMEABILITY OF FACTICE FILMS

Run	Factice Time min.	Resin Added Type	%	Film Weight g./100 sq.in.	Water-Vapor Permeability g./(24 hr./100 sq.in.) Uncreased	Creased
30	45	Rosin-beeswax	50	6.0	0.75	1.08
33	440	Rosin	50	19.5	1.49	1.18
35	120	Piccolyte S-L	50	16.9	2.17	6.57
36	60	Beeswax	50	9.7	0.48	1.56
37	45	Paraffin wax	50	11.1	1.94	2.39
46	65	Vinsol	50	21.0	1.37	1.42
47	30	Meadol	50	11.0	3.75	5.36
39	120	Paraffin wax	100	8.8	1.06	2.86
40	120	Paraffin wax	100	7.9	1.33	1.79
40T	Same as 40, except triplex sheet				0.66	
41	85	Asphalt	100	34.6	0.51	0.58
48	65	Vinsol	100	29.2	0.84	0.81
42	300	Asphalt	200	35.2	0.27	0.28
56	65	Vinsol	300	Film broke on folding		
51*	80	Asphalt	300	20.2	0.21	0.33

* Oil D was used in the preparation of this sample.

Constant Conditions:

30 grams of linseed oil C ($n_D^{37.5}$ 1.4854, viscosity 324)
1.5 grams of sulfur
1.5 grams of C-16

Percentage of resin based on the weight of the oil

Temperature, 145° to 150° C.

in Table IV that 10 per cent of this resin lowered the W.V.P. of the film from 4.2 grams to 3.5 grams. In addition, the factice time was more than doubled. Even 50 per cent of Piccolyte S-40 lowered the W.V.P. to only about 2.0 grams. The factice time was increased more than tenfold.

It was evident that Piccolyte S-40 was not desirable for the modification of the factice films. It had too little influence on the W.V.P. of the film, and hindered factice formation to too great an extent. In addition, sheets laminated with this material possessed a strong pine odor, which would be unsatisfactory for food wrapping.

A special use for this laminating material might be in the production of greaseproof, waterproof, and mothproof bags; the factice would produce the first two qualities and the Piccolyte the third. Factice containing 50 per cent of Piccolyte S-40 was very tacky and sticky and might prove a good substitute for Scotch tape. It would stick to any type of surface and, when the tape was pulled off, would leave a clean, smooth surface.

Piccolyte S-L

This Piccolyte resin was a much more viscous material and possessed less odor than the S-40 resin. The addition of 10 per cent of S-L to the factice gave no improvement in the W.V.P. of the film, but the factice time was almost tripled. The presence of 50 per cent of this resin lowered the W.V.P. to about 2.2 grams, but the sheet had poor folding properties. Folding the sheet at room temperature tripled its W.V.P.

Piccolyte S-L was likewise judged unsatisfactory for the modification of factice films. It decreased the W.V.P. of the film too little and increased the difficulty of vulcanization too much. Laminated sheets containing this product also had an undesirable odor. In large quantities, the presence of the resin ruined the flexibility of the factice film.

Falkyd Resin B-7

Falkyd resin was also a very thick, viscous, semiplastic material. Although clear and odorless, it proved to be of little value in improving the W.V.P. of factice films. From Table IV, it is seen that the addition of 10 per cent or even 50 per cent of this resin had practically no effect upon the W.V.P. of the factice film. It certainly could not be expected to produce a material suitable for water-vapor protection.

Rosin

The rosin employed for experimental purposes was that used for sizing. No trouble was experienced in mixing molten rosin and hot oil. In small percentages (10 per cent), rosin produced an improvement in the W.V.P. of the factice, by lowering it to about 2.5 grams. The addition of 50 per cent of rosin to the factice lowered the W.V.P. to about 1.2 grams. However, the time required to produce the factice was increased from 20 minutes for the oil alone to 440 minutes for the oil and rosin. With a sample containing 100 per cent of rosin, no factice had formed after 10 hours.

It was concluded that, even though rosin did produce an improvement in the W.V.P. of the factice films, the improvement was not great enough in view of the difficulty in preparing the factice. With high percentages of rosin, the factice material became thermoplastic. At temperatures around 145° C., these compounds were fluid; at 0° C., they were hard and brittle. For these reasons, the use of rosin was not considered a solution of the problem of water-vapor resistance.

Rosin-Beeswax

A 50-50 mixture of rosin-beeswax was used in sealing the samples during the W.V.P. tests. It was decided to try this material in a factice compound. A mixture of 10 per cent of rosin-beeswax gave a film having a W.V.P. of about 1.8 grams (creased or uncreased), which was a decided improvement over the pure factice film. The addition of 50 per cent of this rosin-beeswax combination lowered the W.V.P. of the film to approximately 0.8 gram (Tables IV and V). However, upon folding, this value increased to about 1.2 grams. The presence of the rosin-beeswax caused a subsequent increase in the time required to produce the factice and also made it slightly thermoplastic.

It was apparent for several reasons that rosin-beeswax could not be employed to obtain a film with the desired properties. When present in large quantities, the material offered the same difficulties encountered in the use of rosin alone.

Beeswax

It was assumed that the superiority of the rosin-beeswax mixture over pure rosin was the result of the presence of the beeswax. Therefore, factices were prepared which contained various percentages of beeswax. It was found that this material caused a marked improvement in the W.V.P. of the factice film. It was possible to obtain a W.V.P. of about 0.5 gram by adding 50 per cent of beeswax to the factice. The film producing this high resistance was influenced by folding, for the W.V.P. of creased specimens averaged approximately 1.6 grams. Factice containing this percentage of beeswax was quite thermoplastic and possessed a waxy appearance, but lacked the tackiness, flexibility, strength, and resiliency common to pure factice.

Beeswax produced a reasonable improvement in the W.V.P. of factice films, but it was far from ideal. Sheets laminated with factice-beeswax materials did not possess the folding properties common to factice. Furthermore, the supply and cost of beeswax are such that the main purpose for its addition to factice is defeated. One could not make a cheaper and more available product by adding a costly, unavailable material.

Paraffin

A major portion of the paper used for wrapping or packaging is coated, impregnated, or laminated with paraffin wax of some type. Ordinary paraffin wax has such a large crystal structure, even at room temperatures, that it is brittle and will not withstand flexing. It was found that the modification of paraffin wax with factice caused a great reduction in the crystal size of the wax. Using 100 per cent of paraffin, a product was obtained which possessed many of the properties of a microcrystalline wax. The material had a fair degree of flexibility and even some resiliency. Values for the W.V.P. of factice containing 50 per cent of paraffin were about 2.0 grams for the unfolded sample, which increased to 2.4 grams with folding. Increasing the quantity of paraffin to 100 per cent lowered the W.V.P. to 1.3 grams for uncreased samples and to 1.8 grams for the creased samples. The data are given in Table V.

Paraffin wax produced a decided improvement in the W.V.P. of factice films. At the same time, the factice became very thermoplastic, did not withstand folding, and possessed too many of the characteristics of paraffin. It was evident that an entirely different field of wax modification could have been studied. However, in view of the scarcity of waxes and the promising results obtained by the use of other materials, the investigation was not continued. It is possible that a higher density, smoother finished kraft sheet would have given even better results. White factice might be more desirable for the modification of paraffin waxes, because it would not produce a deep red color.

Vinsol

Vinsol is a cheap, available plastic material which might find use in work of this kind. Investigation proved that Vinsol would produce a good improvement in the W.V.P. of factice materials. The addition of 50 per cent of Vinsol to factice gave a product having a W.V.P. of about 1.4 grams for either creased or uncreased samples. If the quantity of Vinsol was doubled (100 per cent), this value was lowered to 0.8 gram. Even in this quantity, Vinsol seemed to have very little effect upon the folding qualities of the sheet. Increasing the amount of filler to 300 per cent gave a film which was brittle at room temperature and which failed upon folding.

Vinsol proved to be one of the most promising materials used in this study. It is cheap and, in normal times, is readily available. Marked improvements in the W.V.P. of factice films were obtained by its use. However, the optimum ratio of Vinsol which could be employed was 100 per cent. This meant that the laminating material still contained too large a portion of the critical linseed oil. In normal times this product would certainly be given further consideration. Films prepared from it were reasonably flexible, thermoplastic, and water-vapor-proof.

Meadol

Because this commercial lignin (a by-product of soda black liquor) is available in large quantities at a reasonable cost, it was deemed worthy of investigation. However, it was soon found that this product was not desirable as an addition to factice films. The presence of 50 per cent of the material caused no improvement in the W.V.P., but it did produce a dark substance possessing a distinct odor. Upon aging, the laminated sheet became black and dirty looking. For these reasons it was evident that Meadol is not suitable for the production of this type of laminating material.

Hide Glue

Glue is one of the best greaseproof materials available in large quantities. However, glue films are so brittle that they will withstand no flexing at ordinary temperatures. It was though that, by vulcanization with linseed oil, a soft, flexible, greaseproof product might be obtained. At the same time there might be a marked improvement in the waterproofness of the glue.

Glue is not thermoplastic, so it could not be mixed with the hot oil in the usual manner. For this reason, a special method of preparation had to be developed. It was soon found that a very thick aqueous solution could be prepared by adding large quantities of glue to hot water. This aqueous solution was easily emulsified with the oil, accelerator, and sulfur used for vulcanization. The vulcanization process in this case had to be carried out at 100° C. The water was gradually boiled from the emulsion, and the latter became viscous like a factice. The cooking process required several hours. The material was then employed to laminate sheets in the usual manner.

A homogeneous product, very light in color, was thus obtained. The laminated sheet had to be oven dried for a short time to remove the remaining water. Sheets laminated with the material were not as flexible as desired if large quantities (100 per cent) of glue were used in the preparation. Although the water resistance of the glue was improved, sheets would separate after soaking for 3 hours. No tests for W.V.P. were made on these samples.

Asphalt

Asphalt is the most widely used laminating material for water and water-vapor protection. However, its effectiveness in this application is greatly impaired by its thermoplastic character. If the water-vapor resistance of asphalt could be combined with the flexibility of factice, a very desirable product might result. The asphalt used in the investigation was a 200° F. melting point, ground asphalt.

Asphalt was combined with factice in amounts varying from 10 to 300 per cent. The actual effect of the asphalt on the W.V.P. of the factice film is given in Tables IV and V. Even when present in relatively small amounts, the asphalt produced a great improvement in the W.V.P. When present in large quantities (300 per cent), a soft, flexible product was obtained having a W.V.P. of 0.2 gram. This was superior to any results thus far obtained.

It was concluded that asphalt seemed the best solution to the problem of an addition material for factice. Asphalt is very cheap and readily available. Products containing high percentages of asphalt were slightly thermoplastic at 145° C., just enough to make lamination easy. They possessed excellent water-vapor resistance, and were soft, flexible, and resilient even at low temperatures. It seemed evident that a factice-modified asphalt material was worthy of a detailed investigation.

SUMMARY

The presence of Piccolyte resins, Falkyd resins, rosin, Meadol, and rosin-beeswax, in combination with factice, did not produce a suitable laminating material. In general, they caused relatively slight improvement in the water-vapor permeability of factice films, and often the films possessed objectionable odors or brittleness.

Paraffin and beeswax can be employed to modify factice with fair results. However, these materials are too unavailable and costly for large-scale production under present conditions. The use of factice to product a microcrystalline wax would be of great interest for other products.

Vinsol gave a product possessing good water-vapor protection, but it could not be added to the factice in large quantities without producing a brittle film. Such a material would require a high ratio of unavailable linseed oil.

Asphalt could be mixed in very large quantities with linseed oil, the resulting mixture vulcanized with sulfur, and a product obtained which was soft, flexible, resilient, waterproof, and water-vapor resistant. The material was slightly thermoplastic, was very suitable for laminating purposes, possessed only a slight odor, and showed reasonable flexibility at low temperatures. Because asphalt is available as a cheap raw material in very large amounts and because asphalt-laminating equipment is in general use, it was concluded that this product should be subjected to a detailed investigation.

PART III

A STUDY OF THE VARIABLES IN THE PRODUCTION OF A FACTICE-MODIFIED ASPHALT-LAMINATED SHEET

A STUDY OF THE METHOD OF PREPARATION

In view of the facts presented in Part II, it was concluded that the modification of factice with asphalt, or asphalt with factice, would produce a laminating material suitable for large-scale production and useful as a protection against water and water vapor. The factice-modified asphalt sheets described in Part II possessed very desirable qualities of flexibility, resiliency, and water-vapor resistance. The addition of small quantities of factice to asphalt seemed to bring about decided changes in the nature of the latter. The modified material was tacky, tough, very flexible, and even possessed a marked degree of elasticity and resiliency. The change was quite evident by merely comparing the "feel" of factice-modified asphalt with plain asphalt. It was assumed that this change was produced by the presence of the vulcanized oil, and this was confirmed by experiment.

First, an attempt was made to vulcanize asphalt alone, using the conditions employed for vulcanizing a mixture of linseed oil and asphalt. A sample of asphalt was mixed with 10 per cent of sulfur and 5 per cent of C-16 accelerator, heated to 145° to 150° C., and vulcanized for 8 hours. During this time, none of the usual changes experienced in the preparation of factice-asphalt mixtures took place. There was no increase in the viscosity of the liquid; at the end of the 8-hour period, the asphalt was as thin and fluid as it was at the beginning of the process. The material was allowed to cool and stand for several days. At the end of that time the surface of the asphalt was completely covered with "bloomed" sulfur, proving that little or none of it had entered into chemical combination with the asphalt. The resulting asphalt was more brittle than the original, or at least showed no marked improvement. Although the vulcanization of asphalt was known to be possible under certain conditions, it was concluded that the conditions used for the vulcanization of activated linseed oil were not suitable for the vulcanization of asphalt alone. It was apparent that the improvement in physical properties had not been achieved because of the vulcanization of the asphalt.

Raw linseed oil (20 per cent) and asphalt (80 per cent) were then mixed, 10 per cent of sulfur and 5 per cent of accelerator were added (based on the weight of the oil), and the mixture was vulcanized for 8 hours at 145° to 150° C. The addition of the linseed oil increased the fluidity of the asphalt; the long period of vulcanization caused little or no increase in the viscosity of the mixture. Upon cooling, a material was obtained which was softer than the original asphalt but which possed a very oily texture. The only result was that the disadvantages of asphalt had been increased: its softening point had been lowered, and its penetration or bleeding at higher temperatures had been increased. The experiment shows that activated oil is necessary to produce any improvement in the asphalt during vulcanization.

The nature of the vulcanization process was further studied by the use of a mixture containing 20 per cent of highly blown linseed oil and 80 per cent of asphalt. This highly blown oil was thick and jelly-like. The mixture was heated at 145° to 150° C. for 1 hour with constant stirring, but no sulfur was added. It proved impossible to disperse the gelled linseed oil in the asphalt. It was thus evident that the desired results could be obtained only by the vulcanization of the oil in the presence of the asphalt.

Next, a sample of factice was prepared using the standard method given in Part I. At the time factice formation took place and a thick viscous material was being formed, molten asphalt was added to the factice. This method of preparation also proved unsuccessful, because the factice would not disperse in the asphalt and a lumpy product resulted.

It was concluded from this group of experiments that, in order to obtain the desired results, it was necessary to vulcanize an activated oil in the presence of the asphalt, the two materials being thoroughly mixed during the operation. It was further concluded that the improvement of the physical characteristics of the asphalt was due entirely to the presence of the vulcanized oil, and that satisfactory results could be obtained in no other manner.

As a result of this investigation, the general method of preparation described in Part II was adopted. Sheets were laminated and tested using the methods given in that section. All the values for water-vapor permeability are averages of results for at least two and sometimes three specimens.

DISCUSSION OF THE VARIABLES INVOLVED

Influence of Oil Activity

Factice Time. In the discussion of factice-modified asphalts, the time factor might more properly be termed "cooking time." The presence of increasing quantities of asphalt increased the thermoplastic nature of the material and, at the same time, decreased the viscosity of the final product. It has been shown that the activity of the oil was directly connected with the factice time, and that the vulcanization of the oil caused the change in the asphalt. It follows directly from these two facts that the factice time of a factice-modified asphalt depends upon the activity of the oil. This will be discussed in detail under cooking time.

Water-Vapor Permeability. Since the factice-modified asphalt-laminated sheets were of interest primarily as a protection against water vapor, the effect of the activity of the oil on the water-vapor permeability of the final laminated sheet was of great importance. This investigation was extremely difficult because so many uncontrollable variables of lamination and testing existed between the time the factice-asphalt was ready for lamination and the finished sheet had been creased and tested for water-vapor permeability. These variables were kept at a minimum by attempting to control the temperature and viscosity of the factice-asphalt prior to lamination, by employing a constant pressure on the rolls during lamination, and by using the same testing methods. It was impossible to secure a constant film thickness during lamination.

Laminated sheets were prepared using oils of all the various activities in the factice-asphalt material, and employing three sulfur contents for vulcanization. The results of this series of tests are given in Table VI. Because the film weights of the various samples varied to such a great extent, it is impossible to draw any conclusions from these data. It was decided to plot the variation in water-vapor permeability caused by differences in film weight. Figure 7 represents the values for Oils 219-222 (with 5 per cent of sulfur) plotted as described above. The numbers accompanying the points indicate the oil used in the preparation of that particular sample. It is seen that there is apparently no order to the oil numbers. The curves indicate nothing more than a decrease in water-vapor permeability with an increase in the thickness of the film. Figure 8 is a plot of the oils vulcanized with 10 per cent of sulfur and Figure 9 shows the values obtained using 15 per cent of sulfur.

It was concluded from the curves of Figures 7, 8, and 9 that, within the limits of experimental accuracy and for all practical purposes, the activity of the oil had no effect upon the water-vapor permeability of sheets produced from it. The variations of sheet weight and water-vapor permeability of the creased samples prepared with 15 per cent of sulfur were soslight that no curve could be drawn through them. For this reason, they are not plotted in Figure 9.

General Physical Properties. Because the activity of the oil is an important factor governing the physical characteristics of factices, it was logical that a similar effect would be observed with

TABLE VI

THE EFFECT OF OIL ACTIVITY AND SULFUR CONTENT UPON THE WATER-VAPOR PERMEABILITY OF FACTICE-MODIFIED ASPHALT FILMS

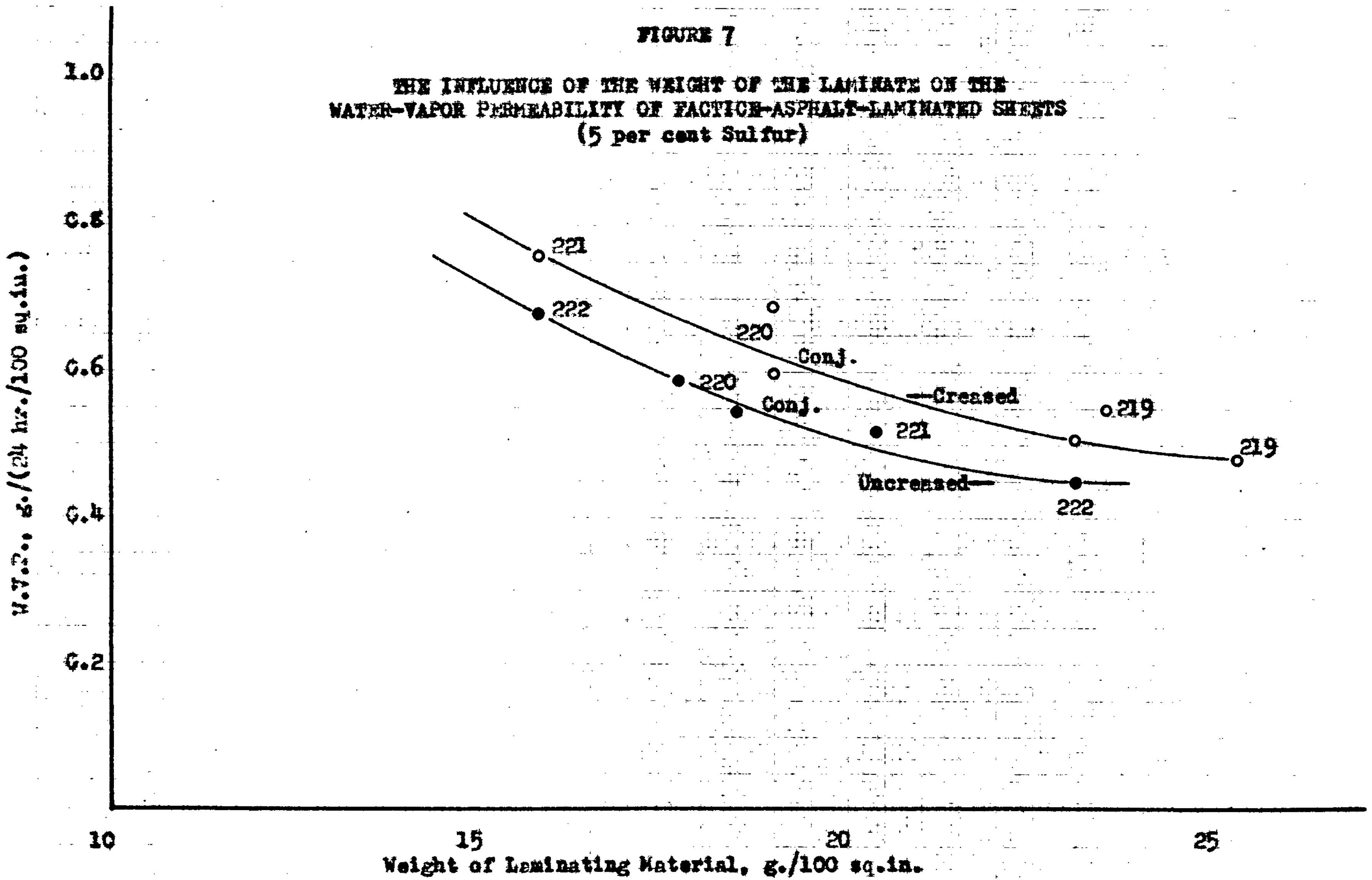
				Uncreased Samples		Creased Samples	
Run	Oil	Cooking Time min.	S %	Film Weight g./100 sq.in.	Water-Vapor Permeability g./(24 hr./100 sq.in.)	Film Weight g./100 sq.in.	Water-Vapor Permeability g./(24 hr./100 sq.in.)
201	222	90	5	23.1	0.45	23.1	0.51
202	222	15	5	15.8	0.68	25.8	0.57
203	221	40	5	20.4	0.52	15.8	0.76
204	220	60	5	17.7	0.59	19.0	0.69
206	Conjulin	60	5	18.5	0.53	19.0	0.59
207	219	120	5	23.5	0.55	25.3	0.48
208	222	20	10	20.8	0.56	15.8	0.83
209	221	25	10	23.1	0.50	15.4	0.79
210	220	35	10	17.6	0.58	16.7	0.76
211	219	55	10	15.4	0.75	12.2	0.98
212	218	80	10	22.2	0.47	18.1	0.69
219	222	15	15	22.2	0.52	17.2	0.74
218	221	17	15	15.8	0.71	14.0	0.88
217	220	30	15	26.2	0.46	15.8	0.88
216	219	30	15	15.8	0.79	14.5	1.03
215	218	55	15	18.1	0.73	14.5	0.96
214	217	70	15	19.4	0.70	14.9	0.91
213	216	90	15	26.7	0.44	14.5	0.71

Constant Conditions:
15 grams of oil
60 grams of 200° F. melting point asphalt
1.5 grams of C-16

Percentage of sulfur based on the weight of the oil alone
Temperature, 145° to 150° C.

FIGURE 7

THE INFLUENCE OF THE WEIGHT OF THE LAMINATE ON THE WATER-VAPOR PERMEABILITY OF FACTICE-ASPHALT-LAMINATED SHEETS (5 per cent Sulfur)



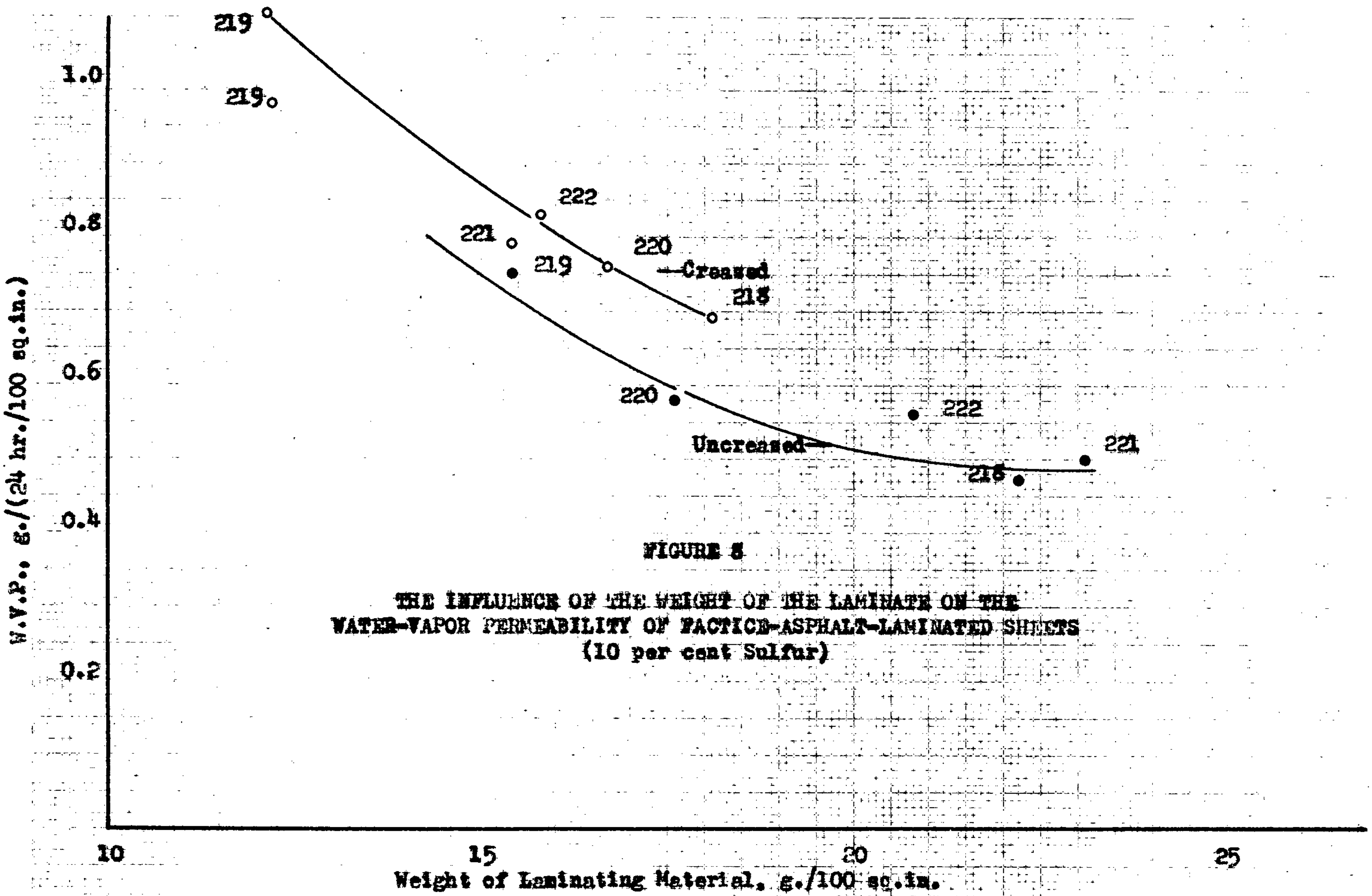


FIGURE 8

THE INFLUENCE OF THE WEIGHT OF THE LAMINATE ON THE
WATER-VAPOR PERMEABILITY OF FACTICE-ASPHALT-LAMINATED SHEETS
(10 per cent Sulfur)

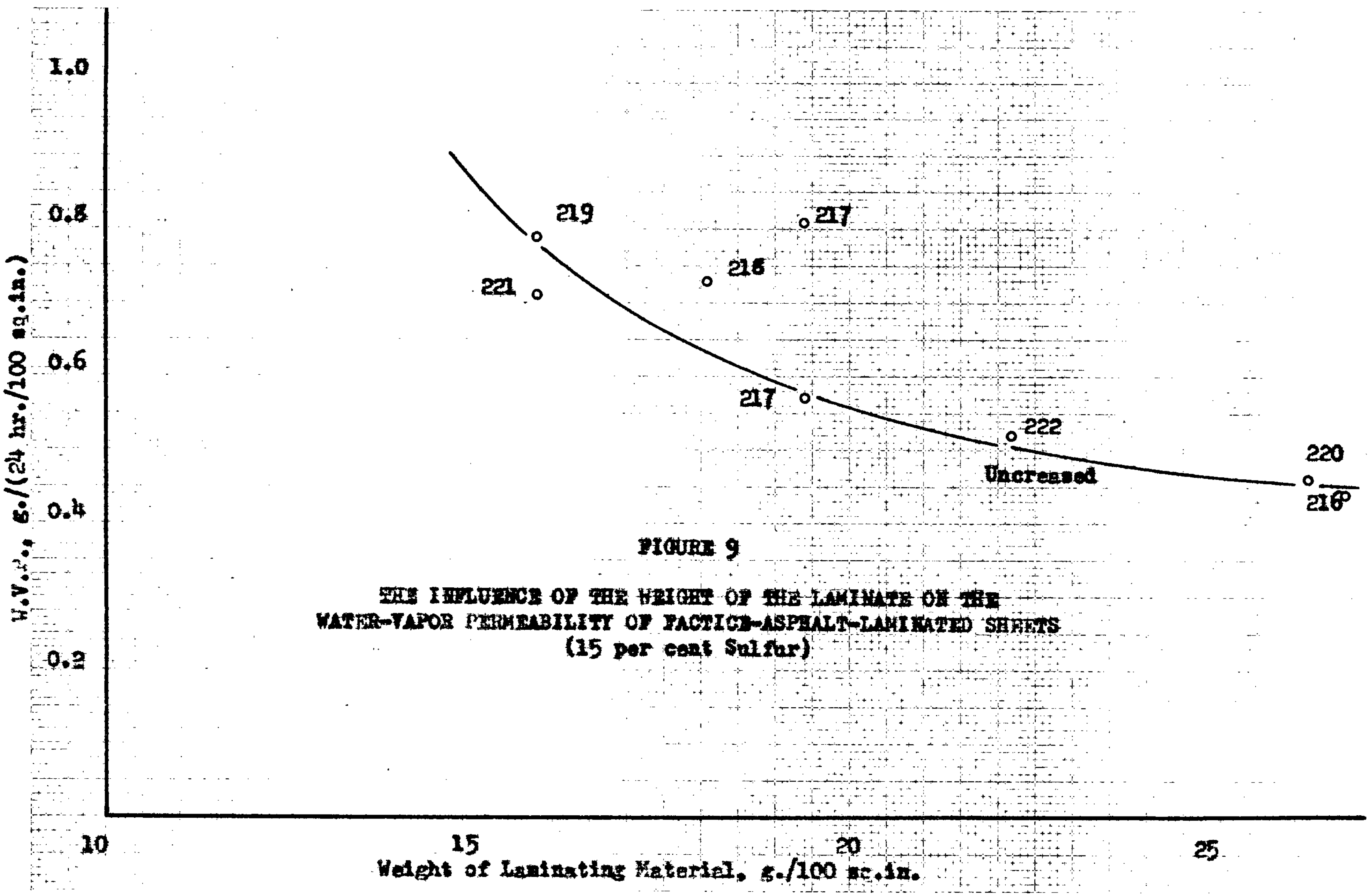


FIGURE 9

THE INFLUENCE OF THE WEIGHT OF THE LAMINATE ON THE WATER-VAPOR PERMEABILITY OF FACTICE-ASPHALT-LAMINATED SHEETS (15 per cent Sulfur) factice-modified asphalts. This was, of course, a direct result of the characteristics of the factice. The more highly activated oils (15-minute factice time) gave factice-asphalt materials which were less thermoplastic at high (100° C.) but less flexible at low (-35° C.) temperatures. For the best general results, the medium activated oil discussed in Part I proved most successful. Sheets laminated with products prepared from them possessed good flexibility and resiliency. The slightly activated oils produced sheets which were softer in texture and which had better flexing properties at low temperatures. However, such materials were unsuited for work in the higher temperature range (80° C.). These oils also gave the factice-asphalt material a slight odor, characteristic of the factice alone.

Influence of Sulfur Content

Factice Time. The influence of increasing the sulfur-to-oil ratio has been discussed in detail on page 33. In general, the same fundamentals hold for the preparation of factice-modified asphalt. An increase in the sulfur-to-oil ratio decreased the cooking time required. This will be discussed further under cooking time.

Water-Vapor Permeability. It will be recalled that, in the study of the influence of oil activity on the water-vapor permeability of the sheet, various sulfur contents were used. This was done to show the effect, if any, of the sulfur-to-oil ratio employed for vulcanization. The sulfur percentages were based on the weight of the oil alone.

The curves for the uncreased samples shown in Figures 7, 8, and

9 have been superimposed in Figure 10. It is evident from this figure that any increase in the water-vapor permeability of factice-asphalt films caused by higher sulfur ratios was of minor importance. Figure 11 contains the curves for creased samples taken from Figures 7 and 8. The increase in water-vapor permeability of the creased specimens as a result of higher sulfur contents seemed slightly larger.

General Physical Properties. The influence of increasing sulfur content on the physical properties of factice alone has been discussed in detail in Part I. It was apparent that any change in the characteristics of the factice would likewise have an effect on the factice-modified asphalt. From Figures 7 and 8, it is seen that films containing a lower sulfur-to-oil ratio have slightly better folding properties. Other characteristics were not influenced too greatly within the range of usable sulfur-to-oil ratios.

The deciding factor in the determination of the sulfur content of a factice-modified asphalt was the presence of free sulfur. Any excess sulfur present does not take part in the vulcanization process and will crystallize or "bloom" upon standing. The presence of uncombined sulfur would make the product unsuitable for food packaging. At the same time, a very strong sulfur odor is imparted to the finished product. The quantity of sulfur-to-oil ratio should be based on the weight of the oil alone, and should be such that little free sulfur remains on completion of the vulcanization process. The proper choice of sulfur-to-oil ratio has been discussed in detail in Part I.

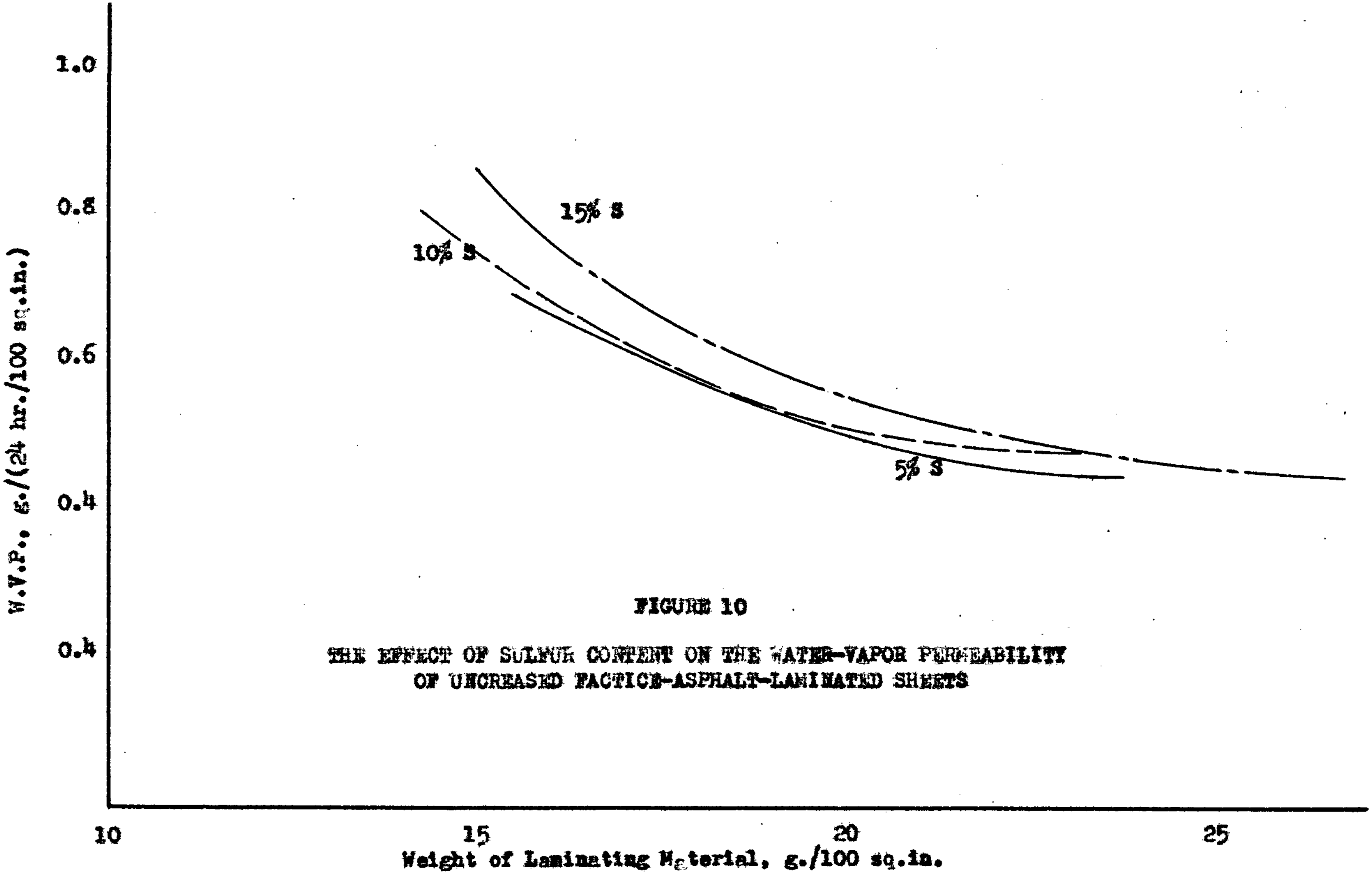


FIGURE 10

THE EFFECT OF SULFUR CONTENT ON THE WATER-VAPOR PERMEABILITY OF UNCREASED FACTICE-ASPHALT-LAMINATED SHEETS

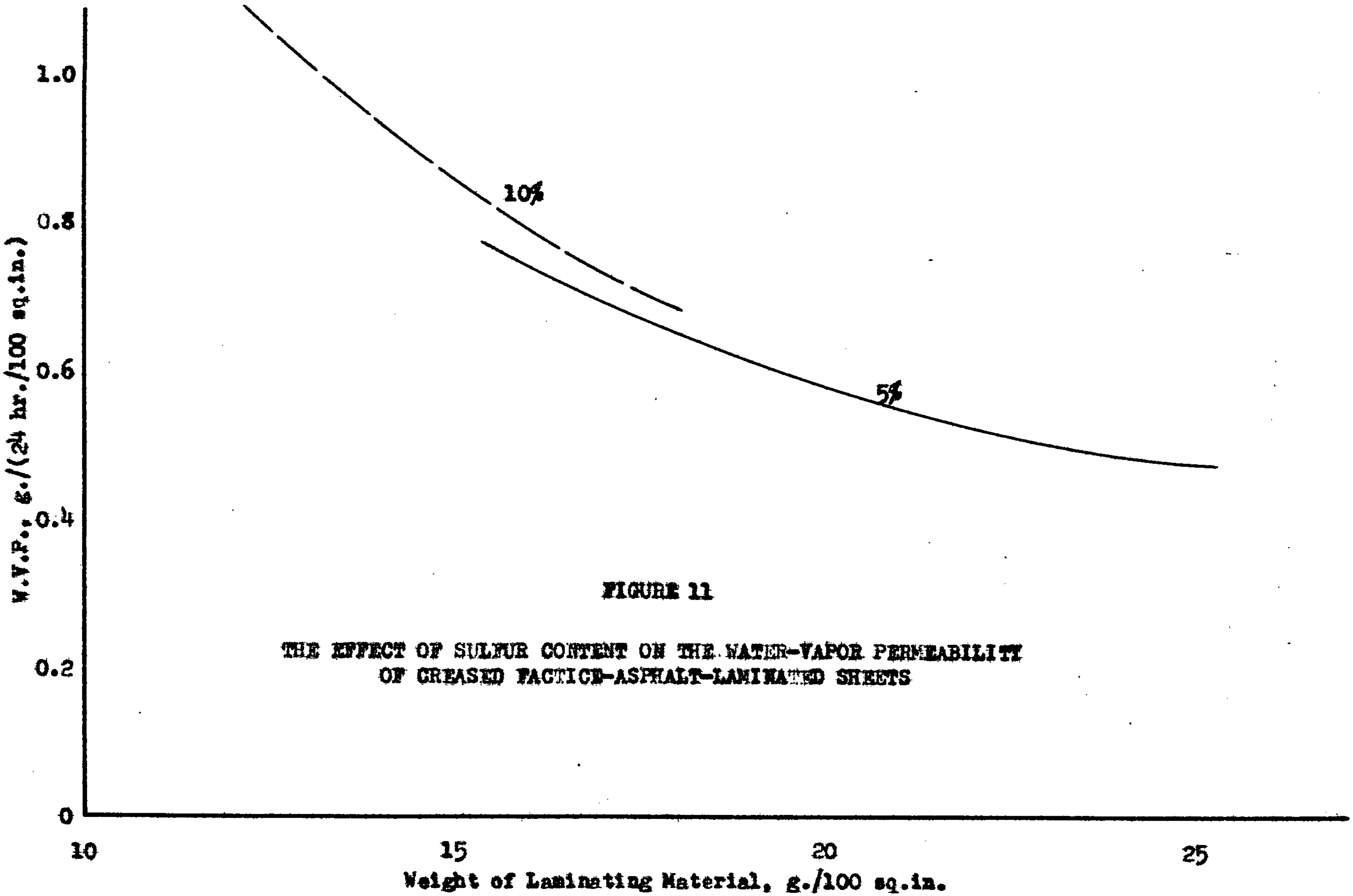


FIGURE 11

THE EFFECT OF SULFUR CONTENT ON THE WATER-VAPOR PERMEABILITY OF CREASED FACTICE-ASPHALT-LAMINATED SHEETS

Influence of Asphalt

In the investigation of the influence of asphalt upon the properties of the factice-modified asphalt product, there were two variables to be studied: the type of asphalt and the quantity of asphalt. It was hoped that, for this portion of the work, five or six asphalt samples, all possessing different melting points, would be available. Because of the prevailing war conditions, however, it was possible to obtain only three types of asphalt. The first was a ground, high melting point asphalt (above 200° F.) used by a board manufacturer. A Standard Oil asphalt, having a softening point of 190° to 200° F., was available in large quantities and was employed for the majority of the work. The only low melting point asphalt was a bituminous road asphalt, which was fluid at room temperature.

Quantity of Asphalt. Most of the investigation of this variable was carried out using the ground or 200° F. melting point asphalt. It was found that pure asphalt alone gave the best resistance to water vapor, and in one case even had good folding properties at 70° F. However, at lower temperatures the film would break. The ratio of asphalt to oil was varied from about 10 per cent to 100 per cent, based on the total weight of the oil and asphalt. The water-vapor permeability of the various samples are given in Table VII.

The data show that the water-vapor resistance of a factice-modified asphalt sheet improved with increasing asphalt content. At the same time, the other desirable properties of the sheet became worse. It was unfortunate that adequate small-scale laminating equipment was

TABLE VII

THE EFFECT OF THE QUANTITY OF ASPHALT ON THE WATER-VAPOR PERMEABILITY OF FACTICE-MODIFIED ASPHALT SHEETS

Run	Oil	Cooking Time min.	Asphalt Type	Asphalt %	S %	C-16 %	Film Weight g./100 sq.in.	Water-Vapor Permeability g./(24 hr./100 sq.in.) Uncreased	Water-Vapor Permeability g./(24 hr./100 sq.in.) Creased
22	C	50	Ground	9.1	5	5	13.6	3.27	
25	C	50	Ground	16.7	5	5	10.2	2.26	2.46
27	C	75	Ground	33.3	5	5	17.4	1.00	1.81
41	C	85	Ground	50.0	10	5	34.6	0.51	0.58
42	C	300	Ground	66.7	10	5	35.2	0.27	0.28
51	D	80	Ground	75.0	20	5	20.2	0.21	0.33
54	D	60	200° F.	75.0	20	5	17.2	0.48	0.53
52	D	115	Ground	85.7	40	10	21.2	0.20	Film broke
55	D	90	200° F.	85.7	40	10	17.4	0.32	0.31
220		0	200° F.	100.0	0	0	20.3	0.23	0.29
S.R.*			200° F.	100.0	0	0	17.8	1.44	7.86

* A commercially laminated sheet used in multi-wall bags

Percentages of sulfur and C-16 based on the weight of the oil alone.

Percentage of asphalt based on the total weight of the asphalt and oil.

not available so that constant laminating conditions could have been secured. Values could then have been obtained at constant film weights, and the variation of water-vapor permeability with different asphalt contents plotted.

Although the presence of increased quantities of asphalt produced a desirable change in the water-vapor resistance of the laminated sheets, it was accompanied by undesirable changes in the physical characteristics of the final product. A sheet laminated with pure asphalt would withstand folding fairly well at 70° F., but at -30° F. it was so brittle that it would break and shatter like glass with a very slight degree of flexing. Sheets containing only 20 per cent of factice would withstand a quick 180-degree fold at -30° F. around a diameter of 1/4 inch without failure. At room temperatures, the factice-modified asphalt sheet had much more flexibility, resiliency, and soft texture. Increasing the amount of factice in the material increased the flexibility and gave better folding properties. At the same time, the performance at higher temperatures (180° F.) was improved. The thermoplastic properties of the product increased with increasing asphalt content.

The above results might be summarized by stating that the factice-modified asphalt film is dependent upon the asphalt for its water-vapor resistance and upon the quantity of factice for its flexibility, elasticity, resiliency, and working-temperature range. The ratio between the two must be governed by the temperature range in which the product finds application, the cost and availability of linseed oil, the degree of flexibility, and the water-vapor resistance desired.

Type of Asphalt. The type of asphalt used in the production of factice-modified asphalt was of importance from the standpoint of physical properties and water-vapor resistance. As has been stated before, three types of asphalt were available. It was found that the best water-vapor resistance was obtained with the highest melting-point asphalt. Typical results secured with the three grades of asphalt are given in Table VIII.

TABLE VIII

THE EFFECT OF THE TYPE OF ASPHALT ON THE WATER-VAPOR PERMEABILITY OF FACTICE-MODIFIED ASPHALT-LAMINATED SHEETS

Type	Amount Added %	Film Weight g./100 sq.in.	Water-Vapor Permeability g./(24 hr./100 sq.in.) Uncreased	Creased
Road Asphalt	80	26.2	0.71	0.76
200° F. melting point	80	23.1	0.45	0.51
Ground	75	20.2	0.21	0.33

These results (quoted from Table VI and Table VII) give the general increase in water-vapor permeability obtainable by lowering the melting point of the asphalt used. Tests were not made to determine whether the water-vapor resistance of sheets laminated with these asphalts alone varied in the same order. It is seen that a factice-asphalt mixture containing 25 per cent of factice (based on the total weight of factice and asphalt) had as good water-vapor resistance as was obtained with the 200° F. melting point asphalt alone. Once again, the desirable physical characteristics were produced by substances causing lower water-vapor resistance. For soft, flexible, resilient sheets, the lower melting point asphalts were more desirable. Sheets laminated with factice prepared from road asphalt would withstand a 180-degree fold with pressure at a temperature of -30° C., which was a decided improvement over products prepared from the ground asphalt. However, the former showed more penetration and bleeding at a temperature of 50° C. For products to be used in the high temperature range (60° to 100° C.), the higher melting point asphalts proved most desirable.

From the above discussion, it is evident that the choice of type and quantity of asphalt employed in the production of factice-modified asphalts depends upon the use requirements of the application. Products can be developed to fit any desired characteristics, following the general variables outlined above. For any specified asphalt, vulcanization with increasing quantities of oil will result in a widening of the temperature range of application, increased flexibility and folding properties, and lower water-vapor resistance.

Effect of Accelerator

The quantity and type of accelerator might also have an effect upon the character of factice-asphalt films. No study of this variable was made.

Influence of Temperature

The effect of temperature upon the formation of factice from linseed oil has been discussed previously. Its influence upon factice-modified asphalt would be of concern only in so far as it changed the character of the factice. For the most part, all the vulcanizing was performed at 145° to 150° C., although it was found that this temperature could be increased to 165° to 170° C. without any deleterious effect on the final product. If the temperature of cooking was allowed to rise much above 200° C., localized overheating and burning of the material resulted. This produced an undesirable "burned" smell and should be avoided. In addition, the final product had a brittle quality.

Influence of Time

The cooking time required to produce a suitable factice-modified asphalt was not as definite as the time necessary to vulcanize linseed oil alone. If the mixture contained over 25 per cent of oil, the usual factice end point was encountered. This was indicated by a rapid increase in the viscosity of the mixture, and the final product was a semifluid mass. With lower quantities of oil and higher percentages of asphalt, the end point was not as definite. There was a gradual thickening of the mixture until the final product had the consistency of molasses. The presence of large quantities of asphalt with the oil increased the time required for the completion of the vulcanization. In larger scale operations, this difficulty was overcome by giving the oil a prevulcanization treatment before the addition of the asphalt. In this manner the oil molecules were in better contact with each other, and polymerization took place more quickly.

In the vulcanization of small quantities of oil (20 grams) and asphalt (80 grams), a cooking time of 2 to 2.5 times the factice time of the oil proved optimum. A comparison of the factice times of Table I and Table VII will show this to be true. If the factice formation of the oil alone occurred in 20 minutes, the factice-asphalt mixture was cooked for 40 minutes. The factice-asphalt mixture could be undercooked—that is, incompletely vulcanized—but it could not be injured by overcooking. If the temperature did not rise above 165° C., the material could be kept hot for 24 hours with no apparent change. This was a decided advantage over factice, which stiffened and changed with prolonged heating. The material could be cooled, kept for days, and then reheated without loss in flexibility. For these reasons, it proved desirable to cook the factice-asphalt combination longer than the minimum time required for vulcanization.

Effect of Film Thickness

It was shown previously in this section that the results obtained in the study of the influence of oil activity and sulfur content were in reality the effect of film thickness on the water-vapor permeability of the finished sheet. Figures 7, 8, and 9 illustrate this variable. No further study of this variable was made with the inadequate laminating process.

In later work discussed in Part IV, the effect of film thickness on water-vapor permeability was investigated using a semi-commercial laminating machine. It was shown that a small increase in the film weight caused a great improvement in water-vapor resistance at low film weights, but with heavy film thickness the improvement was not noticeable. Figure 12 illustrates the results of this work, which is discussed in detail in Part IV.

Variables of Lamination

Optimum laminating conditions were not obtained by the use of a clothes wringer; therefore, the variables could not be studied. It was assumed that the water-vapor resistance of the sheet would depend upon film thickness, film continuity, and penetration. The less the penetration into the sheet, the better would be the water-vapor resistance of the film for a given weight of laminating material. Impregnated sheets, in general, proved to be poor barriers to water vapor. Penetration of the lamination material would depend upon the type of sheet, the temperature and viscosity of the laminating material, the temperature and pressure of the squeeze rolls, and the speed of lamination. These variables are discussed in greater detail in Part IV. In this case, the lamination was carried out on a semi-commercial machine and the variables were more easily controlled.

SUMMARY

The best results in the preparation of a factice-modified asphalt were obtained by vulcanizing a suitably activated oil in the presence of molten asphalt at a temperature of 145° to 150° C. for a time interval equal to twice that required for the oil to form a factice alone, similar ratios of sulfur and accelerator being used.

The vulcanized oil was responsible for the improved characteristics of the asphalt. Vulcanization of the asphalt or the mere addition of unvulcanized oil did not produce the same results.

The activity of the oil employed for vulcanization influenced only the physical characteristics of the factice-modified asphalt sheet and had no influence upon the water-vapor resistance of the latter. Slightly activated oils produced factice-modified asphalts more suitable for low temperature applications; highly activated oils were best for high temperature uses.

The amount of sulfur used in the vulcanization of a factice-modified asphalt was governed by the oil alone. An increased sulfur content produced slight increases in the water-vapor permeability of the films and poorer folding qualities. High sulfur contents were accompanied by a disagreeable sulfur odor.

The type and quantity of asphalt employed in the preparation of factice-modified asphalts had a definite influence on the properties of the material. The higher melting point asphalts gave better water-vapor resistance than the low melting point asphalts, but the products possessed less flexibility. Pure asphalt proved to be the best water-vapor barrier; increasing percentages of factice caused subsequent increases in water-vapor permeability, but gave better flexibility. The choice of the type and quantity of asphalt employed in the production of a suitable laminating material depended upon the temperature range covered in its use requirements, the flexibility desired, the water-vapor resistance necessary, and the allowable cost of production. For low temperature work, low melting point asphalts and high oil ratios were desirable. For high temperature uses, high melting point asphalts and high oil ratios proved best.

Localized overheating above 200° C. caused a burning of the factice-modified asphalt and gave a disagreeable "burned" odor.

Factice-modified asphalts were unaffected by prolonged heating for 24 hours, if the temperature was kept below 165° C. The material could be cooled and reheated without injuring its desirable qualities.

By the proper choice of asphalt, oil activity, and oil-to-asphalt ratio, products can be made which will withstand 180-degree folds at -30° C., or which will not bleed at 100° C. Treatment by this process would improve the desirability of any asphalt available.

PART IV

SEMICOMMERCIAL PRODUCTION AND APPLICATION OF FACTICE-MODIFIED ASPHALTS

As stated previously, the object of this investigation was the preparation of a laminating material suitable for large-scale, heavy-tonnage production methods and possessing definite advantages over the available materials. A product may show great promise in the laboratory stage, but in large-scale production some insurmountable obstacle appears and the project has to be discarded. Although the laboratory tests on the factice-modified asphalts seemed to indicate a definite application of the material, its true value could not be judged until at least semicommercial operations had been tried. In this case the quantities were changed from grams to pounds, and finally to hundreds of pounds. Semicommercial laminating equipment was available at the Institute; no other special apparatus was necessary.

It was unfortunate that this semicommercial investigation was undertaken before a more complete knowledge of all the variables of factice-modified asphalt production had been gained. The preliminary study had given a method of preparation of a material and, although the exact variables of its production were not thoroughly understood, sufficient knowledge was available for the preparation of a good, usable product. It was decided that the purposes of the investigation could be expedited by trying a commercial application of the material in its preliminary form. If the material seemed as usable and desirable after a short semicommercial search, then time would be taken to study more fully the details of activation and vulcanization. This is exactly what was done. Although this work appears last in this dissertation, chronologically it was undertaken before a great majority of the material previously presented.

METHOD OF ACTIVATION

Because the semicommercial application of the product was attempted before all the work on the activation of the oil had been completed, the oil was activated by heating at a temperature of 350° C. About 20 pounds of raw linseed oil in a stainless steel bucket were placed on a 1000-watt hot plate and heated, with stirring, to 350° C. The time required to reach maximum temperature was about 2 hours in every case. Bunsen burners were used to heat the sides of the bucket, making this rapid increase in temperature possible. The oil was held at maximum temperature for 30 minutes, removed from the hot plate, and allowed to cool to room temperature. After cooling, the suitability of the oil was tested by vulcanizing a small sample with 5 per cent each of sulfur and accelerator. The time for factice formation varied between 20 and 35 minutes and was judged suitable for the process. It can be seen that this method of activation and control was crude, as compared with the process developed later and discussed in Part I. The method proved effective, although the activity of the oil was difficult to control and was far from a constant value.

VULCANIZATION PROCESS

It was known that the presence of the asphalt increased the time necessary for vulcanization. Using the Vanderbilt C-16 accelerator, it was necessary to boil the water from the oil-water emulsion before the asphalt could be added. Such an operation required only a moment when small quantities were involved; however, in treating several pounds of oil, the cooking time necessary to remove the water was much greater. This proved to be an advantage rather than a disadvantage. A partial vulcanization of the oil took place during the initial heating period. Because the oil was not mixed with asphalt, it was much easier for the polymerization to start. There was not sufficient sulfur present in the accelerator (C-16) to cause complete curing of the oil, and therefore it was not necessary to be concerned about overcooking. When several pounds of the oil were treated, the prevulcanization was continued for about 1 hour; if 15 to 20 pounds of oil were involved, the time increased to 1-1/2 hours. The prevulcanization process proceeded as follows.

The desired amount of activated oil was weighed into a stainless steel bucket, placed on an ordinary small gas stove, and the heating process started. Agitation of the oil was accomplished by means of a Lightnin mixer. Immediately after the heating had been started, the necessary quantity of C-16 was added slowly, care being taken that the latter dispersed throughout the oil and formed the proper emulsion. The heating was continued until the oil reached a temperature of 100° C., at which point the water started boiling from the emulsion and foaming occurred. The temperature was maintained at 100° C. until all the water had evaporated from the oil, and then was increased to 145° C. The oil was vulcanized at this temperature for about 1 hour. The total time of the prevulcanization was approximately 1-1/2 hours.

Meanwhile, the required amount of asphalt was melted in a 5-gallon pail (a 50-gallon drum was used when large quantities were prepared) and heated to 145° C. The asphalt was also stirred by means of a Lightnin mixer. The prevulcanized oil was then mixed with the molten asphalt, the sulfur added, the the vulcanization continued until it was complete.

If the factice-asphalt mixture contained over 20 per cent of oil, a definite factice end point was observed. If the percentage of oil was 10 or 15 per cent, the final product possessed the viscosity and appearance of molasses. This has been discussed in Part III. The final vulcanization was carried on for 1 to 2 hours, depending on the activity of the oil used. In Run 65, it was necessary to continue the final vulcanization for a longer period of time, because Oil H had not been activated properly.

The end point of the reaction could be identified by changes in the physical characteristics of the mixture. When vulcanization was about completed, the mixture assumed a smooth, homogeneous texture. Small samples, on cooling, no longer had an "oily" feeling. The material was soft, flexible, and resilient. Immersion in cold water did not change these properties. Under such treatment, asphalt would become hard and brittle. With a little experience any operator could judge when vulcanization was complete. At any rate, as has been discussed in Part III, overcooking did not injure the final product. The factice-asphalt mixture had to be well agitated during vulcanization, to avoid localized heating and to obtain a homogeneous product.

The ratios of asphalt, oil, sulfur, and accelerator used in these four semicommercial runs are given in Table IX. The percentages of oil were based on the total weight of the oil and asphalt, whereas the percentages of sulfur and C-16 were based on the weight of the oil alone. It will be observed that unusually high sulfur contents were employed and, as a result, Run 58 had an objectionable sulfur odor. In each of the subsequent runs, the sulfur content was lowered. It was evident from the work carried out later, and presented in Parts I and III, that 5 per cent sulfur would have been sufficient.

The ratio of C-16 appears to be an odd figure. This was the result of an error in calculating (changing pounds to grams) the weight of C-16 necessary to give 5 and 10 per cent of accelerator. The amounts actually employed were 6.7 and 13.4 per cent.

LAMINATING PROCESS

A semicommercial laminating machine available at the Institute was used to form the factice-asphalt combined sheet. The lamination process itself was very simple. Two sheets of 20-inch kraft paper were passed from reels at the ends of the laminator (one reel at each end) to the two 24-inch, horizontal squeeze rolls in the center of the machine. The two sheets passed over the tops of the squeeze rolls and ran vertically down between the rolls. At this point the two sheets were combined by the factice-asphalt mixture. The combined sheet was then conducted over several guide and unheated drier rolls to a reel. The factice-asphalt material (145° C.) was poured from a bucket into the nip between the squeeze rolls during the operation. The rolls were steam heated. Very satisfactory, continuous films were obtained in this manner.

Such a method of lamination permitted better control, and several variables could be studied which could not be investigated by the laboratory technique of lamination. The film weight and penetration could be controlled by the pressure on the squeeze rolls, the temperature of the rolls, the type of paper being laminated, and the speed of lamination.

In Run 58, a very soft waterleaf kraft sheet was used for laminating. During this process, the temperature of one squeeze roll was 240° F. and that of the other was 170° F. This difference in roll temperature caused a decided variation in the penetration of the factice-asphalt into the sheets. In neither case was the penetration appreciable. In subsequent runs, both rolls were heated to 170° F.

Runs 59 and 60 were made using a regular asphalting paper produced by a commercial asphalting mill. It was a more dense sheet, possessing a much smoother finish than the waterleaf kraft. In Run 65, the paper laminated consisted of a special kraft sheet used in the production of multi-walled bags. Its surface texture and general characteristics were better than the waterleaf but not as good as the other kraft sheet.

The distance between and the pressure on the squeeze rolls were governed by two adjustable bolts which pushed one roll against the other. This adjustment proved to be very delicate, particularly during the lamination of very light-weight sheets. Oftentimes the speed of the machine was increased to vary further the weight of laminating material between the sheets.

Sheets laminated with several basis weights of factice-asphalt were produced in every run. These sheets were tested for water-vapor permeability as described before, and other special use-requirement tests were made. A large roll of laminated paper produced in Run 65 was sent to an eastern mill to be converted into bags.

USE-REQUIREMENT AND OTHER TESTING RESULTS ON THE MACHINE-LAMINATED PAPER

The laminated papers produced in the semicommercial operation were obtained in sufficient quantities and sizes to permit a variety of tests.

Water-Vapor Permeability

Table IX contains the results of the water-vapor permeability tests on these samples. It is seen that, by using larger scale methods, it was possible to duplicate the promising results obtained in the laboratory.

Sample S.R. was a commercially laminated asphalt sheet. The improvement of the factice-modified asphalt over pure asphalt is very evident. Equal weights of laminating material would give about as good water protection when uncreased, and much better when creased. Samples 59A and 58A show this very definitely. If the oil content was increased to 20 per cent, it was necessary to apply a slightly heavier film to

TABLE IX

WATER-VAPOR PERMEABILITIES OF FACTICE-MODIFIED ASPHALT SHEETS LAMINATED ON A SEMICOMMERCIAL MACHINE

Run	Cooking Time	Oil	Oil %	Sulfur %	C-16 %	Film Weight lb./ream*	Water-Vapor Permeability g./(24 hr./100 sq.in.) Uncreased	Water-Vapor Permeability g./(24 hr./100 sq.in.) Creased
58A	75	E	11.1	40.0	13.4	60.0	0.82	0.82
58B	75	E	11.1	40.0	13.4	71.4	0.70	0.73
58F	75	E	11.1	40.0	13.4		5.64	7.76
59A	120	E	11.1	28.8	13.4	41.7	1.14	1.65
59B	120	E	11.1	28.8	13.4	118.5	0.44	0.49
59C	120	E	11.1	28.8	13.4	147.0	0.34	0.41
59H	120	E	11.1	28.8	13.4	51.0	1.35	3.14
60A	60	E	20.0	20.0	6.7	32.7	2.10	4.55
60B	60	E	20.0	20.0	6.7	59.2	1.49	1.52
60C	60	E	20.0	20.0	6.7	166.0	0.39	0.44
60D	60	E	20.0	20.0	6.7	248.0	0.27	0.31
65A	210	G&H	20.0	20.0	6.7	74.5	0.99	1.11
65B	210	G&H	20.0	20.0	6.7	45.0	1.55	2.00
S.R.**			0	0	0	35.0	1.44	7.86

* Ream size was 24x36—480.

** S.R. was a commercially laminated asphalt paper.

obtain the same water-vapor resistance but the folding qualities of the sheet were improved very greatly. Samples 60B and 65A illustrate this fact. The influence of increased asphalt content on the water-vapor permeability of the product has been discussed in detail in Part III.

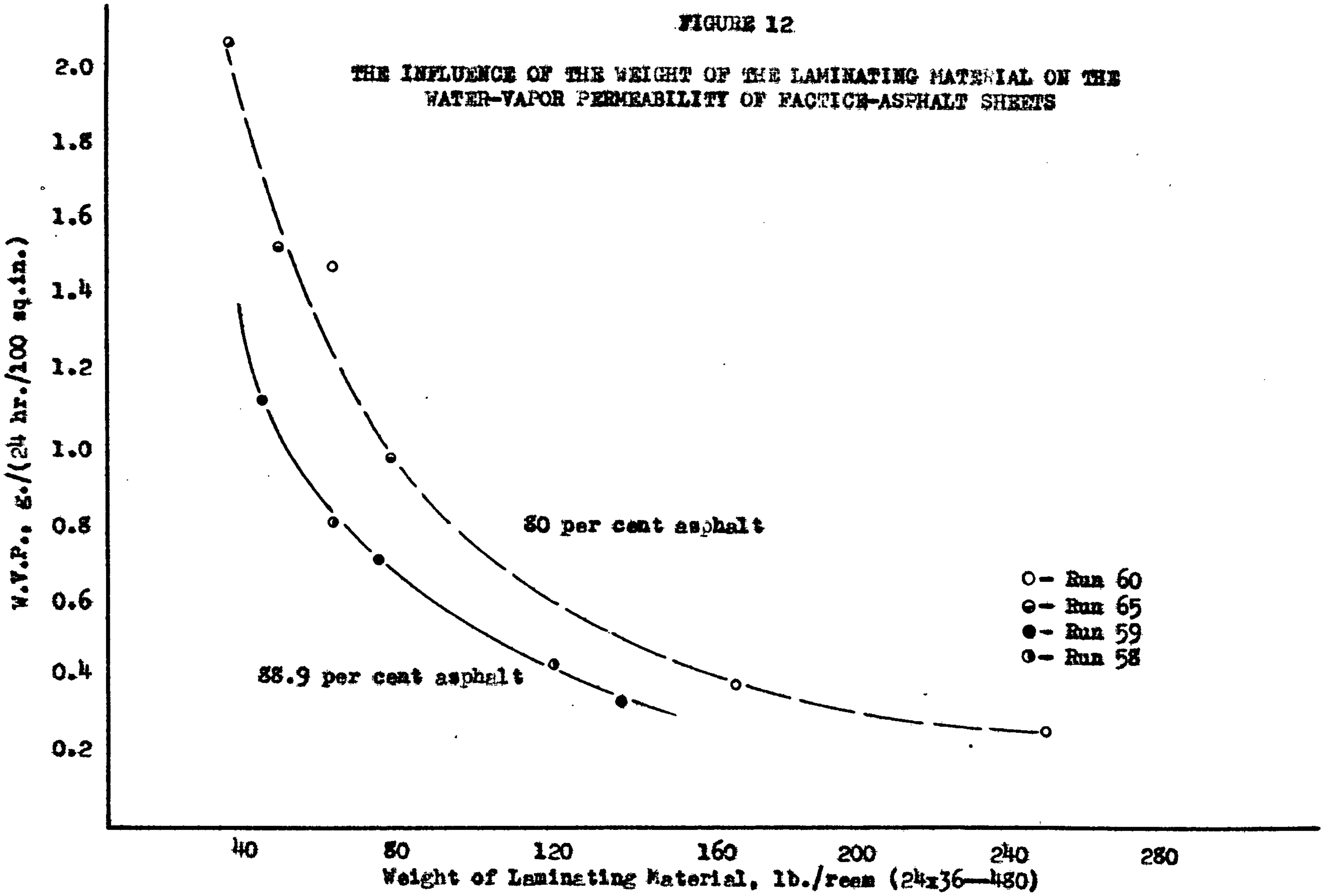
The harmful effect of overheating the factice-asphalt material before lamination is shown in Sample 59H. The laminating material remaining at the end of Run 59 was allowed to become overheated and burned by cooking for a short period above 200° without agitation. The product possessed a "burned" smell and, when used to combine paper, gave a higher water-vapor permeability for the uncreased sheet and much poorer folding qualities. This proved more conclusively the injurious effect of overheating, which has been discussed previously.

Variation of Water-Vapor Permeability with Film Thickness

This variable has been discussed in Part III but, because of the crude laminating methods used in small-scale operation, it could not be studied adequately. The data given in Table IX for the variation of water-vapor permeability with film thickness have been plotted in Figure 12. The curves show that a very slight increase in the weight of laminating material was of great importance with laminate weights below 100 pounds per ream (24x36—480). Slight increases in the thickness of a heavy film caused very little change in the water-vapor permeability. The folding qualities of the paper were all very good as long as a continuous film existed between the sheets. The cost and desired water-vapor resistance were the deciding factors in the film thickness in a factice-asphalt-laminated sheet. The high flexi-

FIGURE 12

THE INFLUENCE OF THE WEIGHT OF THE LAMINATING MATERIAL ON THE WATER-VAPOR PERMEABILITY OF FACTICE-ASPHALT SHEETS



bility of the product made it possible to increase the film thickness and still retain its folding properties—an impossible operation with ordinary asphalt.

Figure 12 also indicates the improved water-vapor resistance obtained by using higher percentages of asphalt. This has been discussed in Part III.

Flexibility

Sheets manufactured on the semicommercial apparatus possessed the same high degree of flexibility, resiliency, and folding properties characteristic of the laboratory products. Folding at ordinary temperatures had little influence upon the water-vapor resistance of the film. Small pieces of the factice-asphalt materials were placed in the snow for several hours and were found to be soft and flexible. Under the same conditions, asphalt was brittle and broke upon flexing.

Small samples of the laminated paper were placed in the cold box at -30° C. and tested for flexibility. Sample 65A proved the best for low temperature work. The reason for this was evident after the remaining work on the problem had been completed. This sample contained the highest ratio of oil to asphalt, the least activated oil, and the lowest ratio of sulfur to oil; all these factors gave better low temperature operation. Even the thicker films would withstand a great deal of flexing at this temperature. Care had to be taken in making this test, or the sample would heat up before the flexing took place. Folding was carried out in the cold box; the operator wore gloves, and the samples were grasped by the ends and flexed quickly through 180 degrees. The sample used for testing was 5 inches long and 1 inch wide. In each case the radius of curvature of bend was of the order of 1/8 of an inch.

The most drastic test for flexibility and folding properties of the sheet was performed on a previously conditioned sheet 4 inches square; conditioning was carried out in a constant humidity room at 50 per cent relative humidity and 70° F. The 4-inch square was wadded into a ball about 1/2 inch in diameter, and a 24-pound weight was placed on the ball for 10 seconds. Then the sheet was smoothed out and tested for water-vapor permeability. Such drastic treatment increased the water-vapor permeability of Sample 55 (Table VII) from 0.32 gram to 0.94 gram per 24 hours per 100 square inches. Similar treatment increased the values for Sample 54 from 0.48 gram to 1.10 grams per 24 hours per 100 square inches. Samples 58A and 58B contained lower percentages of oil and lighter films and, therefore, were influenced more by the above-mentioned treatment. The increases of these two were 0.73 gram to 4.13 grams and 0.82 gram to 3.81 grams per 24 hours per 100 square inches, respectively. Even after such drastic treatment, the latter two samples still had twice the water-vapor resistance possessed by the commercial asphalt paper creased in the usual manner.

Water Immersion Tests

One of the most urgent problems to be solved during the prevailing conditions was a method for waterproofing and water-vaporproofing cartons used for export purposes. An outside wrapping which would be resistant to water and water vapor seemed to be the logical solution to the problem. The protection afforded by a factice-modified asphalt layer was tested in two ways.

Six small boxes (5-1/4 by 3-1/4 by 4-1/4 inches), filled with scrap iron, were tested. A thin coat of hot factice-asphalt was applied to the outside of three of the boxes, and the boxes were wrapped in kraft paper while the factice-asphalt was still hot. This method in reality laminated an outside kraft liner to the boxes. The three remaining boxes were wrapped with paper prepared in Run 60C. The seams of the wrapping were fastened and sealed with hot factice-asphalt material.

After wrapping, the boxes were immersed in a tank of water and left for 7 days. Every day the boxes were handled to see whether any noticeable loss in strength had occurred. At the end of the 7-day period, the boxes were removed from the soaking tank, unwrapped, and examined. Not one single soft or swollen part existed on any of the boxes, indicating that no water had passed the sheet.

To test for further water-vapor resistance, three of the boxes were filled with 8-mesh, technical-grade calcium chloride, weighed, and wrapped in the same manner with paper from Run 60C. The ends and seams were again sealed with factice-asphalt. After being immersed for 4 days in water, the boxes were removed and the excess water was blotted from the outside cover so that none of it would come in contact with the box during unwrapping; the boxes were then unwrapped and weighed. The original weights ran between 700 and 800 grams, and had been obtained with an accuracy of 0.2 gram. With this accuracy it was impossible to detect any increase in the weight of the four samples. It was concluded that at least no great amount of water vapor had passed the protective wrapping.

Freezing Tests

Containers for foodstuffs are often subjected to quick freezing operations to preserve their contents. During the short period of time while they are being moved from the freezer to refrigerator cars or to distribution depots, these cartons often come in contact with hot, humid air. The water vapor in the air quickly diffuses into the carton, condenses, and immediately destroys the strength of the box. If this water vapor could be prevented from reaching the box, such failure would not result.

Two boxes were filled with calcium chloride as before, weighed, wrapped in paper from Run 600, sealed with factice, and subjected to the following schedule:

From 8 a.m. to 4 p.m., they were placed in a constant humidity room at 50 per cent relative humidity and 70° F. From 4 p.m. to 8 a.m., they were kept in a cold box at -35° C.

After being treated for 7 days in this manner, the boxes were placed in a constant humidity room at 95 per cent relative humidity and 100° F. for a similar length of time.

At the end of the 14-day treatment, the boxes were unwrapped and weighed. The following results were obtained: Box A gained 2.90

grams; Box B gained 2.50 grams. The total surface of the box was 110 square inches, so the average rate of penetration of the water vapor into the box was 2.70/(14 x 1.10) or about 0.18 gram per 24 hours per 100 square inches. Judging from these results, the factice-modified asphalt-laminated sheet gave adequate protection even under the most severe conditions.

High Temperature Tests

None of the sheets produced in the semicommercial runs showed any tendency toward bleeding when aged for several weeks at 100° F. Samples from Runs 60 and 65, kept in an oven at 105° C. for 10 to 15 minutes, gave evidence of only very slight traces of bleeding. The products containing the higher oil-to-asphalt ratios proved more suitable for high temperature applications. Normal temperature ranges (up to 150° F.) had no effect upon the samples.

Sample 58F (Table IX) was produced by heating Sample 58A at 125° C. for 30 minutes. The heating process caused the sheet to be impregnated by the laminating material. The final product was a glossy, shiny, smooth-finish, black product possessing very good water resistance, but very poor water-vapor resistance. This material was still flexible enough to withstand creasing, had no odor, and might be used for notebook covers or for other applications where water-resistant papers are desired.

Multi-Wall Bags

As has been stated before, the paper laminated in Run 65 was produced for an eastern manufacturer of multi-wall bags. A sizable roll of paper made during this run was ultimately converted into bags for testing. The numerical results of the testing are not available, but the material was reported to be well suited for this work and field tests are to be made in the near future.

Reclaiming Factice-Modified Asphalt-Laminated Sheets

The reclaiming of the fibers from factice-modified asphalt sheets would present a number of problems. The soft, tacky, rubber-like characteristics so desirable for use requirements would make it difficult to be reused. It would stick and clog the beater rolls, would be hard to break up, and would offer much trouble on the paper machine. The only possible method of separation might be to screen the factice-asphalt material from the fibers. Some work was done on the reclaiming of the fibrous material. Small pieces of the laminated paper were soaked overnight and disintegrated with a malted-milk mixer. It was found that the fibers would separate from the film, which remained in large flakes, but only with difficulty. The factice-asphalt material might then be screened from the fibers.

Turpentine Tests

The presence of the large quantities of asphalt decreased the grease resistance of the factice to such an extent it was no longer considered a greaseproof material. Using the Institute turpentine test (21), failure of the semicommercial laminated sheets occurred in about 4 hours. The asphalt proved to be soluble in the turpentine. No other greaseproof tests were made.

OTHER USES OF FACTICE-MODIFIED ASPHALTS

Laminated Boxboard

The work reported previously involved the protection of the boxes by wrapping with laminated paper. In this manner a completely waterproof and water-vapor-resistant package could be obtained. The protective film might, however, be incorporated into the box during construction by laminating the liners with factice-modified asphalt. Export boxes having asphalt liners are being produced, but failure of the box after soaking is very common. This failure occurs at the score along the edge of the box.

Samples of a 100-point virgin kraft export box and of a corrugated board were laminated with factice-asphalt using the following method: A thin coating of factice material was poured on one side of the board, a sheet of kraft paper placed over the factice, and the board and sheet run through a wringer. This produced a kraft liner laminated to the board with an even coat of factice-asphalt. The other side of the boxboard was laminated by the same method.

For testing purposes, the four edges of the laminated and unlaminated board samples were sealed with hot factice-asphalt. In this way the water had to pass through the lateral surfaces of the boards. The samples were immersed in water for a period of a week. After 24 hours, the unlaminated samples had swollen and lost most of their strength; at the end of 7 days, they were falling apart. There appeared to be no loss of rigidity or strength in the laminated samples. It was concluded that adequate protection had been given the board to preserve it for long periods of time. Because of the resiliency and flexibility of the factice-asphalt film, the board would be less affected by the scoring operation than would one containing asphalt alone.

Sealing Air-Conditioning Equipment

It was desired to insulate and seal the air-conditioning equipment used to maintain the humidity rooms. In order to prevent condensation on the equipment during the hot summer months, good water-vapor resistance was needed. The soft Masonite insulating material covering the apparatus was laminated with factice-modified asphalt. The hot, viscous material was applied to the soft layer of Masonite, spread out with a trowel, and another layer of insulating material placed against the film. All the cracks and corners were plugged with the warm material. It proved very desirable for such uses. The final product was soft, rubberlike, resilient, and not tacky. The success of this venture cannot be determined until summer; the protective film may prevent the water vapor from reaching the cooling equipment.

Toluene Solutions of Factice-Asphalt

It was found that toluene would dissolve or at least disperse factice-modified asphalts. Furthermore, after the solvent had been evaporated, the residue seemed to possess all the characteristics of the original material. This made it possible to form factice-asphalt films from a cold solution. For certain applications, this might be more desirable. Concentrated toluene solutions (25 per cent) of factice-asphalt were prepared and used to paint films on paper, employing an ordinary paint brush. Such a thick solution resulted in pinholes and uneven films. When the concentration of the factice-asphalt was lower (10 per cent), suitable films could be obtained by painting or spraying the paper. The film dried quickly, and was very continuous, glossy, and water resistant. A film formed in this manner, which weighed only 18 pounds per ream (24x36—480) and had a water-vapor permeability of 1.7 grams per 24 hours per 100 square inches. Heavier films gave as good water-vapor resistance as the sheets laminated with hot factice-asphalt. For special types of papers, it might be desirable to cast the factice-asphalt film from a solvent.

Waterproofing Rope

One of the problems confronting the Navy Department was the waterproofing of hemp rope. Manila was no longer available, and domestic hemp lost its strength after being in contact with water. It was thought that the factice-modified asphalt might be used to waterproof the hemp cordage. If the water was unable to reach the hemp, degradation would be prevented and the rope would not lose its strength. At the time this thesis was being written, only the preliminary work on the project had been carried out.

Several strands of rope cordage were impregnated by dipping them into a hot factice-asphalt mixture. Several other strands were impregnated with a toluene solution of factice-asphalt. After the films had dried, the strands were soaked in water for 5 days. The actual aging and testing of the treated rope were carried out in connection with another project; hence, these results will be reported elsewhere. However, the soaking caused a great loss in strength of the untreated strands but had little influence on the treated rope. The rope treated with the toluene solution of factice-asphalt gave the better results, probably because of more uniform impregnation. Some fermentation seemed to take place in the aging of the hot treated rope. The strands treated with the toluene solution retained their original strength and showed no fermentation. This opens another field of application for factice-modified asphalt products.

Laboratory Uses

Factice-modified asphalts proved very useful in sealing the edges of plastic-laminated papers for water-absorption tests. The activated oil alone proved to be a very good high-vacuum seal at all temperatures. Two investigators successfully employed it to seal joints and connections in high-vacuum work.

SUGGESTED COMMERCIAL PRODUCTION METHODS AND APPLICATIONS

It has been stressed throughout this dissertation that the variables in the production and application of a factice-modified asphalt are very numerous. The types of materials which can be prepared are almost unlimited. For best results a special product should be developed for each use requirement. This would involve the preparation of many different mixtures. Perhaps the easiest and best method of production could be carried out in a central plant which would manufacture and sell a standardized product for each use requirement. With such a method of distribution, each individual consumer would be spared the trouble of preparing the factice-asphalt mixtures but, instead, could purchase the finished product ready for application. This section has been written from this point of view. However, the same production methods would apply to each individual plant.

Activation of the Oil

The activation of the oil can be carried out in a steam-jacketed kettle carrying a steam pressure of 250 pounds per square inch. The kettle should be equipped with a good agitator and some type of air distributor which will aerate the entire kettle during the cooking operation. Raw linseed oil is placed in the tank and heated to 200° C., observing a definite time-temperature schedule. The time necessary to reach maximum temperature should be as short as can be obtained easily with the equipment. When the maximum temperature has been reached, compressed air is bubbled through the oil. If this aeration is started while the oil is cool, a serious foam problem will be encountered.

During the first few activation runs, the oil should be sampled at regular intervals so that the change in viscosity, index of refraction, and factice time can be followed. The results of these tests would give a family of curves similar to Figures 2, 3, 4, 5, and 6. Such values could be used to set up technical control standards. Having once secured these data, any desired activity of the oil could be obtained by heating to a definite viscosity and then shutting off the steam and air. Although it would require some time for the oil to cool after the heat had been removed, activation would proceed very slowly without the aeration.

A very simple viscosity tube can be constructed from an ordinary 25-ml. pipet, as described in the Appendix. After technical control methods have been set up, the operator can dip a portion of the oil from the tank, allow it to cool to 100° F. (or any temperature taken as standard), and determine the viscosity of the oil. If an Abbé refractometer is available, the index of refraction can also be taken. By reference to the charts, the operator can determine the activity of the oil under treatment.

When the activation process is completed, the steam and air are shut off and the oil is allowed to cool. Under these conditions a suitably activated oil should be obtained in 3.5 to 4 hours. Assuming that the testing was carried out at 100° F. and with apparatus identical with that used in this investigation, the refractive index of the oil should be in the range of 1.4825 to 1.4835 and the relative kinematic viscosity between 85 and 125 seconds. These values are for oils which will form factices in 20 to 30 minutes, using 5 per cent each of sulfur and Vanderbilt C-16 accelerator.

Commercially activated oils are available on the market at the present time, so that it would not be necessary for every mill to have equipment for this part of the process. Conjulin, tested in the experimental program, is an activated linseed oil manufactured by the Woburn Company. The oil proved satisfactory for the preparation of factice-modified materials. However, it is not recommended for general use for several reasons. The cost of the activated oil is too high (about 39 cents per pound) compared with 11 cents a pound for linseed oil. In addition, the oil possesses an undesirable odor which is imparted to all materials prepared from it. In the near future, these two difficulties may be overcome and it may be desirable to purchase the activated oil rather than to produce it in the mill.

Prevulcanization of the Activated Oil

After the activated oil has cooled to about 80° C., it is given the initial vulcanization treatment. This treatment could be carried out in the same steam-jacketed kettle used for the activation. To the oil is added 5 per cent of C-16 accelerator, based on the weight of the oil. The mixture must be well agitated during the addition of the accelerator to insure its complete dispersion throughout the product. The temperature of the emulsion of accelerator and oil is raised to 100° C. and held at this temperature until all the water is boiled off, when the mixture is heated to 145° C. Cooking under these conditions is continued for 1 hour. At the end of this time the oil is ready to be added to the asphalt.

It might prove advantageous to market the activated, prevulcanized oil. This oil could be added to molten asphalt, sulfur introduced, and the final vulcanization carried out at the plant where it is to be used. In this case, the prevulcanized oil could be run into drums for shipment.

Vulcanization Process

The vulcanization of the oil-asphalt mixture is carried out preferably in a steam-jacketed kettle, also equipped with a good agitation devide. The asphalt is melted and is heated to a temperature of 145° to 150° C. while the oil is being prevulcanized. The oil is then added to the asphalt, and the required amount of sulfur is introduced into the mixture. Heating at 150° C. is continued until the vulcanization has been completed. The time of cooking depends upon the activity of the oil, the sulfur-to-oil ratio, and the quantity of asphalt used.

The type and quantity of asphalt depend upon the use requirements of the final product. For high temperatures (180° to 200° F.), a 200° F. melting point asphalt and 20 to 25 per cent of oil would be desirable. For ordinary temperature ranges, a 140° to 160° F. melting point asphalt should be employed. Lower melting point asphalts could be used to obtain products desirable for extremely low temperatures (-35° F.). The quantity of oil required may vary from 5 to 25 per cent of the total weight of the oil and asphalt. For oils in the given range of activities, 5 per cent of sulfur (based on the weight of the oil) should be sufficient. The choice of these materials has been discussed in detail in Part III.

An oil having the activity stated should be completely vulcanized in 1 to 2 hours. Prolonged cooking cannot injure the properties of the product, because the temperature will never rise above 165° C. if a steam pressure of 100 pounds per square inch is used. A definite end point occurs with oil contents of about 20 per cent, as evidenced by a great increase in the viscosity of the mixture. With lower oil contents, the end of the reaction is indicated by the smooth, homogeneous texture of the mixture. The actual cooking time necessary for each factice-asphalt mixture would soon be learned by experience.

Methods of Distribution

After the vulcanization had been completed, the factice-modified asphalt could be pumped into tank cars for shipment to large consumers. These cars are equipped with steam coils to heat the contents so that it could be pumped into the mill. Care would have to be taken to avoid the use of high steam pressures for any of the heating processes, since localized overheating will give the product an odor.

For the small consumer, it would not be desirable to ship the factice-asphalt in small cans or barrels. The material would be difficult to remove without the application of direct heat. It would be much better to cast small briquets or to pack the material in fairly small slabs. This could be accomplished in a number of ways.

The molten factice-asphalt could be poured slowly upon a large, water-cooled, slowly revolving drum. The surface of the iron drum should be plated with a thin coat of tin, which is then amalgamated. The factice-asphalt will not stick to this amalgamated surface, and the cooled mixture can be removed by a doctor blade. The flat sheet thus produced could be cut into slabs, by the use of an amalgamated blade, and sprinkled with talc or given a slight coat of activated oil to prevent the slabs from sticking together; the slabs could then be packed in a carton and shipped.

For some consumers, it might prove more desirable to prepare the material in small briquets weighing several pounds. This could be accomplished by pouring the molten factice-asphalt into small iron molds which have been painted with the activated oil. The presence of the oil prevents the factice-asphalt from sticking to the mold, and leaves a thin film of oil over the surface of the cooled material which removes the tackiness of the briquet. This and the amalgamated surface were found to be the only surfaces to which the factice-asphalt did not stick.

Cost of Production

The present cost of asphalt, raw linseed oil, sulfur, and accelerator used in the production of the factice-modified asphalt is $17.00 per ton, 12 cents per pound, 2 cents per pound, and 50 cents per pound, respectively. Because the cost of the oil is the major item involved, the price of the final product will depend largely upon the percentage of oil employed.

Assuming that the product contains 20 per cent of oil (based on the weight of the asphalt and the oil) and 5 per cent each of sulfur and accelerator (based on the weight of the oil), the total raw material costs for the mixture would be about 3.5 cents per pound. Processing costs might increase this figure to 4 cents per pound.

If only 10 per cent of oil were used (all other values remaining as given above), the laminating compound could be produced at a cost of 2.3 cents per pound for raw materials and a total cost of not over 3 cents per pound.

These figures indicate that the factice-modified asphalt can be manufactured and sold at a reasonable price.

Laminating Process

The factice-modified asphalts can be applied with the equipment now in use for pure asphalt lamination. The material is somewhat thermoplastic and will not harden with reasonable periods of heating, so that application rolls can be employed to spread the material onto the sheet. If the oil content of the compound is high, it might prove more effective to apply the laminating mixture at the nip of the squeeze rolls, as was done in the semicommercial work carried out in this investigation.

The weight of laminating material employed between the sheets would also be governed by the use requirements of the sheet and the allowable cost of production. It was concluded from the experimental work that 70 to 80 pounds per ream (24x36—430) of laminating material were optimum. This gave good folding properties and fairly good water-vapor resistance. For certain applications, this value might be increased.

Suggested Commercial Uses for Factice-Modified Asphalt

Laminated Sheets. The greatest application for a material of this type is in the production of large quantities of laminated papers. The cost of production is low enough so that the material can be employed for the large-scale lamination of cheap kraft papers. In most cases, the substitution of factice-modified acphalt products for the asphalt materials in use at the present time would be a decided advantage. The flexibility, resiliency, and wide temperature range of application make such a product desirable for all types of outside coverings for foodstuffs, machine parts, and chemicals. The material might prove a better laminating medium for the laminated metal-foil bags now employed to obtain the highest degree of water-vapor resistance. For other special applications, sulfite or higher grade papers might be coated with the factice-asphalt dissolved in a solvent.

The production of multi-wall bags opens a large field of application for the material. Bags for the packaging of hot chemicals could be produced, overcoming the danger of bleeding. Bags for low temperature applications could be made from factice-asphalt compositions; these would not be injured by flexing or rough treatment.

Boxboard Uses. A flexible laminated sheet would find many applications in the protection of export boxes. If water and water vapor could be kept away from the box, waterproof adhesives and expensive fillers would be unnecessary. Export boxes could be packed, wrapped in a factice-asphalt-laminated sheet, and sealed with factice-asphalt. After arriving at its destination, the outside wrapper could be removed and the box material repulped. Such a process would involve wrapping equipment not available at the present time.

If repulping of the box after it reached its destination was not of great importance, the outside liner of the box could be laminated with the factice-modified asphalt. Scoring would not cause failure of the film. After the box was packed and the flaps sealed, the three exposed seams on the top and the bottom of the box could be sealed with a piece of kraft tape coated on one side with factice-asphalt. In this manner, the box would again be waterproof.

An alternative of the above procedure might be carried out as a wrapping method. The operation could be carried out on a small table, equipped underneath with a roll of kraft paper, an application roll running in a bath of molten factice-asphalt, and a cutter. The paper would run from the reel, over the top of the application roll, over a guide roll, and up to the top of the table. In this manner, the coated paper would reach the wrapping table with the coated side up. The operator would pull as much paper as he needed, cut it off, set the box in the center of the sheet, and wrap it. The sheet would be self-sealing, and no unsealed seams would remain. By this method the operator would laminate the sheet as he pulled it from the roll. Because the factice-asphalt would be hot, the operator would have to be properly protected. This might be considered a disadvantage of the process.

Wallboards and Insulating Boards. Factice-modified asphalts would find a number of uses in the production of wallboards. Here again, the advantages of a flexible water-vapor-resistant film would be evident. During the winter months such a material would give protection against the passage of water vapor from a warm room through the walls, condensing in the insulation and causing failure. At the time of construction, all the joints and corners could be covered with a narrow kraft tape, coated on one side with factice-asphalt. The tape could be produced with equipment similar to the wetting devices for gummed tapes. Wallboards suitable for outside use could be prepared, the outside liner being impregnated to give it weather resistance.

Roofing Materials. Factice-modified asphalts might find application in the production of asphalt-impregnated roofing papers or felt roofing shingles. It would be possible to produce a material or shingle which would be flexible and not break in cold weather, and still would not be sticky or tacky during the summer. This is one of the important problems confronting the roofing industry. If the application of summer-grade roofing is attempted in the winter, the sheet breaks as the material is unrolled. Likewise, the winter-grade roofing is soft and sticky during the warm months. A factice-asphalt material might be produced which would prove suitable for both conditions.

Factice-modified asphalts might be an improvement over asphalt or "tar" roofs. The factice-asphalt layer would remain flexible over a greater temperature range.

Flooring. A factice-modified asphalt product might be used as a flooring material in basements or places where seepage and similar problems are encountered. The material could be prepared so that it would be flexible and resilient, but neither tacky nor soft. The walls might be coated with the hot mixture to decrease the passage of water through them.

Waterproofing Rope. The preliminary tests on the waterproofing of hemp cordage with a solution of factice-asphalt in a solvent showed great promise. In this manner, the loss of strength and the injurious action of fermentation caused by the water immersion of the rope are eliminated.

Impregnated Papers. It has been shown earlier that, if a factice-asphalt laminated sheet is subjected to a high temperature (125° C.) for about 0.5 hour, the film between the sheets is dispersed and impregnates the entire sheet. The product formed in this manner is very water resistant, possesses a bright, glossy, black finish, and is still flexible. The product has no odor and is not tacky. This material should find application in the production of notebook covers or of small water-resistant boxes for packaging.

Boat-Calking Material. The physical properties characteristic of factice-modified asphalts are such that the material might find use as a calking compound.

SUMMARY

Using semicommercial methods of preparation and lamination, it was possible to produce a factice-modified asphalt-combined sheet possessing the same desirable properties characteristic of sheets prepared in the laboratory. No serious problems were encountered during the entire process, and the product seemed applicable for large-scale operations. The soft, flexible, resilient properties of the sheet remained, and good water-vapor resistance could be obtained.

It proved expedient to employ larger quantities of material for laminating purposes than are generally common with asphalt-laminated sheets. Better water-vapor resistance was obtained without a decrease in flexibility or folding qualities.

Use-requirement tests proved that the factice-modified asphalt could be employed in a number of ways. Export boxes could be wrapped to protect the contents, or the liners could be laminated with factice-asphalt for good resistance against water and water vapor. The same methods could be applied to boxes used in quick-freezing operations. Hemp cordage could be waterproofed and protected from loss of strength with a thin factice-asphalt film.

It was found that factice-modified asphalt could be dissolved or dispersed in solvents such as toluene. Films formed by the evaporation of the solvent possessed good water-vapor resistance and flexibility.

Suggested methods of commercial production and application of factice-modified asphalt products have been given.

PART V

A STUDY OF THE PRODUCTION OF FACTICE FROM TALL OIL

Because of the war conditions, the supply of available linseed oil was rather limited. Since this was the most available of any of the commercially produced oils, the problem could be solved only by turning to a practically unlimited source of noncritical material. Tall oil was such an oil. It could be obtained in almost unlimited quantities, was cheap, and did not have any critical war uses. The production of a suitable laminating material from tall oil would not only have the advantage of a plentiful source of raw material, but would also prove a boon to the pulp industry in the development of a useful product from a waste material. The ideal situation would be for the kraft mills to laminate their paper with a material produced from a by-product of the cooking operation.

EXPERIMENTAL

Commercial tall oil was not available in the immediate vicinity, but some of the soap was collected from a near-by mill.

Because the soap of tall oil would not melt upon heating, it was necessary to dissolve it in boiling water. The material was very soluble. The aqueous solution thus obtained was acidified with dilute sulfuric acid and the tall oil (resin and fatty acids) liberated. Separation of the oil and water was accomplished by filtration.

The small quantity of oil obtained by the above method was activated by heating to 350° C. for 20 minutes. After activation, 30 grams of the oil were vulcanized with 5 per cent each of sulfur and C-16 accelerator. A factice formed in about 15 minutes which had a very light tan color and was soft and flexible when warm, but brittle at room temperature. Although the production of factice materials from tall oil seemed possible, the proper conditions of vulcanization had to be investigated.

If a method for the production of a suitable laminating material could be devised using crude tall oil as the raw material, the process would be much more desirable. It was with this view in mind that a commercial crude tall oil was obtained in sufficient quantities for a detailed study. The product was a viscous, dirty, black oil, containing a large quantity of partially crystallized material, probably the resin acids. The composition of the mixture was given as:

Rosin acids	46.0%
Fatty acids	46.0%
Sterols	7.6%
Moisture	0.2%
Ash	0.32%
Acid number	164.

One sample (tall oil A) was activated by heating, with stirring, 800 ml. of the crude oil to 250° C. in 15 minutes, holding this maximum temperature for 15 minutes, and allowing the oil to cool to room temperature. Vulcanization of this oil with 5 per cent each of sulfur and accelerator at 145° C. did not form a factice in 2 hours; therefore, the oil was considered improperly activated.

A second quantity of the crude oil (tall oil B) was heated to

280° C. in 45 minutes, kept at this maximum temperature for 45 minutes, and allowed to cool to room temperature. A considerable amount of volatile constituents was given off at this temperature, and once the oil flashed and caught fire. Samples of tall oil B were heated for 2 hours with 5 and 10 per cent each of sulfur and C-16. The oil did not become viscous in either case. Upon cooling, a thick sticky mass was obtained. It was concluded that some vulcanization had taken place, but not to a sufficient degree. Further activation of the oil might help to accelerate the vulcanization reaction.

A third portion of the tall oil (tall oil C) was activated by heating to 280° C. in 45 minutes as before; this temperature was held for 10 minutes until most of the volatiles had been removed, after which the temperature was increased to 350° C. and held at this maximum for 60 minutes. The total activation time was 2 hours. After cooling, 30 grams of tall oil C were vulcanized with 1.5 grams each of sulfur and C-16, using the regular procedure described in Part I. At regular 30-minute intervals additional 1.5-gram portions of sulfur were added, until a total of 6.0 grams of sulfur was mixed with the oil. Vulcanization at 145° C. was continued for 4 hours. At the end of this time, the oil was still not thick like a factice. The mixture was allowed to cool until it was approximately as viscous as factice, and sheets of kraft paper were laminated as discussed in Part I. This run was designated as Run 400.

Another 30 grams of tall oil C were vulcanized with 6.0 grams of sulfur and 1.5 grams of C-16, using the standard method of preparation.

Vulcanization at 145° C. was continued for one hour, after which sheets were laminated as described above. This was called Run 401.

Run 402 was carried out by adding 6.0 grams of linseed oil 222 to 24 grams of tall oil C and vulcanizing the mixture for 2 hours at 145° C., using 2.0 grams of C-16 and 3.0 grams of sulfur. Even the addition of 20 per cent of the highly activated linseed oil did not cause factice formation. The mixture was allowed to cool before sheets were laminated.

DISCUSSION OF RESULTS

Only a few days were available for the work on tall oil, but during that time no satisfactory products were prepared. The presence of the high percentage of resin acids probably caused the difficulty of factice formation. It will be recalled from Part II that the addition of only 50 per cent of rosin (based on the weight of the oil alone) to highly activated linseed oils made factice formation almost impossible. It seemed logical that the rosin was again responsible for the slow vulcanization. Because rosin is thin and fluid at high temperatures and crystalline and brittle at low temperatures, it imparts these undesirable properties to the factice. Furthermore, the presence of the resin acids may have made the activation of the fatty acids more difficult. It was concluded that tall oil would not prove a substitute for linseed oil in factice-modified asphalts, unless the resin acids were removed. Any purification of the tall oil would increase its cost to such an extent that it would lose its advantage over linseed oil.

A suitable laminating material might be produced from tall oil alone, if the variables of activation and vulcanization were studied more completely. This material would probably fail in extremely low or high temperature ranges, but might prove useful at ordinary temperatures.

Samples of Run 400, 401, and 402 were placed in the hot room at 100° F. for water-vapor permeability testing. Samples 401 and 402 became so soft that the laminating material impregnated the sheet, giving it a sticky surface. These sheets were not tested, because the film had been broken.

The water-vapor permeability of Sample 400 was 0.4 gram per 24 hours per 100 square inches for a sample containing 34.4 grams of laminating material per 100 square inches. Creased samples were not tested. This indicated the good water-vapor resistance possible with a film of vulcanized tall oil.

SUMMARY

The presence of the high percentage of resin acids in crude tall oil makes it unsuitable as a possible substitute for linseed oil in factice-modified asphalt materials.

A laminating material suitable for use in a very restricted temperature range, but possessing good water-vapor resistance, could probably be produced by the vulcanization of crude tall oil.

CONCLUSIONS

From a study of the variables involved in the production and application of factice prepared from linseed oil, the following conclusions were drawn.

A factice suitable for laminating purposes can be prepared by the vulcanization of a properly activated linseed oil with sulfur.

The oil can be activated by heating at 350° C. or at a lower temperature for a longer period of time. Aeration permits the lowering of this temperature to 200° C. without an increase in the activation time.

From the index of refraction, viscosity, and method of activation of an oil, it is possible to predict accurately the time required for factice formation, the optimum sulfur necessary for vulcanization, and the general character of the factice produced.

For a given temperature and sulfur and accelerator ratio, the time of formation and physical character of the factice depend upon the activity of the oil.

For a given temperature, oil activity, and sulfur ratio, the time of formation and physical character of the factice depend upon the type and quantity of accelerator added.

For a given temperature, oil activity, and accelerator content, the time of formation and physical character of the factice depend upon the sulfur-to-oil ratio. This ratio is of greatest importance with the slightly activated oils, but of much less importance with highly activated oils.

For a given oil activity and sulfur and accelerator ratio, the time of factice formation depends upon the temperature of vulcanization.

The presence of Piccolyte resins, Falkyd resins, rosin, Meadol, and rosin-beeswax does not produce suitable laminating materials in combination with factice.

Paraffin and beeswax can be modified to a microcrystalline structure by combining them with factice. These materials would be of interest for special uses.

Vinsol can be employed to improve the water-vapor resistance of factice materials, but at the same time it introduces undesirable properties.

The properties of factice which make it desirable for laminating purposes are as follows: (1) The softy, tacky, rubbery film retains its properties independent of temperature conditions. (2) Factice-laminated sheets possess good aging properties, irrespective of temperature. (3) Factice-laminated sheets are greaseproof to mineral, lard, and vegetable oils, as well as to turpentine. (4) Sheets laminated with factice are waterproof. (5) Properly prepared factice has little or noodor. (6) Factice can be prepared easily from relatively cheap raw materials with very little equipment.

The undesirable properties of factice for use in laminating are as follows: (1) Commercial application might present difficulties in view of the tacky, sticky, and nonthermoplastic character of the material. (2) The cost and availability of linseed oil is limited because of the war conditions. (3) Factice-laminated sheets do not have good resistance to the passage of water vapor.

From a study of the variables and properties of factice-modified asphalts, the following conclusions were drawn.

A material, suitable for laminating purposes and possessing a high degree of water-resistance and water-vapor resistance, as well as other desirable qualities, can be prepared by the vulcanization of a properly activated linseed oil in the presence of large quantities of asphalt.

The increase in flexibility, resiliency, elasticity, and other physical properties of the factice-modified asphalts is the result of the vulcanized oil and cannot be obtained unless the properly activated linseed oil is vulcanized in the presence of the asphalt. The results cannot be duplicated by mixing factice and asphalt after vulcanization, by vulcanization of an unactivated oil with the asphalt, by vulcanization of the asphalt alone, or by the addition of activated oil to the asphalt without vulcanization.

The factice-modified asphalts are dependent upon the properties of the factice for their physical characteristics, and upon the type and quantity of asphalt for their water-vapor resistance.

High melting point asphalts produce materials with better water-vapor resistance but less desirable physical characteristics. Low melting point asphalts give better physical properties but less water-vapor resistance.

An increase in the ratio of vulcanized oil to asphalt in a factice-modified asphalt is accompanied by a subsequent increase in flexibility, resiliency, elasticity, and water-vapor permeability of the product.

The activity of the linseed oil used in vulcanization has little or no influence upon the water-vapor permeability of the finished product. However, it is an important factor in the physical character of the material.

Higher sulfur-to-oil ratios in the vulcanization process produce slight increases in the water-vapor permeability of the factice-modified asphalts; at the same time a decrease is noted in the resiliency, flexibility, and other properties of the film. High sulfur contents produce an undesirable sulfur odor in the product.

The vulcanization time of the oil in the presence of the asphalt depends upon the activity of the oil, the sulfur-to-oil ratio, the type and quantity of accelerator, and the oil-to-asphalt ratio. Continued heating for the periods of time necessary in laminating operations has no injurious effect upon the product.

An increase in vulcanization temperature is accompanied by a decrease in the vulcanization time. Temperatures above 200° C. give a burned odor to the product, cause a loss in water-vapor resistance, and tend to make the product brittle. A vulcanization temperature between 145° to 165° C. seems optimum.

By the proper choice of oil activity, oil-to-asphalt ratio, type of asphalt, and sulfur-to-oil ratio, waterproof and water-vapor-resistant materials can be produced which will withstand a high degree of flexing at -30° F. and which will not bleed at 200° F.

The low cost of raw materials and processing of a factice-modified asphalt, the equipment required for its production and application, and the properties of the resulting materials make it very desirable for large-scale production methods.

The flexibility, waterproofness, and water-vapor resistance of the material make it desirable for use in many laminating operations, for the waterproofing of rope, and for other applications requiring these properties.

APPENDIX

MEASUREMENT OF RELATIVE KINEMATIC VISCOSITY OF ACTIVATED OILS

The viscosity of linseed oil undergoes a very rapid change during the activation process. For this reason, the range covered in the measurement of oils of various degrees of activation is very large. Activated oil also becomes rather dark in color, particularly when activated at high temperatures; therefore, viscosity measurements by such methods as the falling ball type are not suitable. The viscosity of activated linseed oil is not truly Newtonian, because much "structural viscosity" or plastic flow is involved. For these reasons, the majority of the usual viscosity measurement methods are not satisfactory.

For plant control methods, exact values of viscosities are of little interest. The apparatus should be cheap, easy to operate, and involve little upkeep. These requirements can be fulfilled by constructing a very simple capillary-type viscometer from a standard pipet. This piece of equipment proved capable of distinguishing oils of all degrees of activation.

Apparatus

The tip of a standard 25-ml. pipet was cut off and the end fire polished until all the rough edges had been removed. However, care was taken to avoid closure of the end to form a small orifice. After fire polishing, the stem of the pipet had approximately a constant diameter. The glass tubing above the body or chamber of the pipet was shortened to a length of about 2 inches. Since the calibration mark on the particular pipet used in the investigation was less than 1 inch above the body of the instrument, this was taken as the standard head for the viscosity measurements.

A collapsible rubber bulb (the type employed to fill burets) was connected by a short piece of rubber tubing to the top stem of the apparatus. The rubber tubing was closed by means of a pinch clamp.

The viscosity tube was held in a vertical position by means of a Bunsen clamp supported by a ring stand. Small 10-ml. volumetric flasks were used to measure the effluent from the viscometer.

Operation

All viscosity measurements were carried out in a constant temperature room at 100° ± 0.5° F. The oils and apparatus were placed in the room several hours before use, so that temperature equilibrium would be reached.

The viscosity tube was filled by placing the lower stem in the liquid, squeezing the air from the rubber bulb, fastening the latter to the pipet by means of the rubber tubing, and allowing the oil to be sucked into the pipet as the rubber bulb assumed its original shape. When the body of the pipet was full and the level of the liquid was above the calibration mark, the rubber tubing was closed with the pinch clamp and the rubber bulb removed.

The excess liquid clinging to the stem of the viscometer was blotted off, and the liquid level was lowered to the calibration mark by carefully opening the pinch clamp, thus allowing part of the liquid to drip from the tube. With very viscous materials it was necessary to wait a short time after leveling the head of the liquid, to allow for the settling of the liquid clinging to the walls of the upper stem.

The tip of the viscometer was then lowered into a 10-ml. volumetric flask. The end of the stem protruded into the wide section of the flask, so that the oil would not flow down the neck of the flask as it dripped from the viscometer. This precaution was unnecessary when liquids of low viscosities were measured.

The pinch clamp was opened, and the time required for 10 ml. to drain from the viscometer was measured. After the liquid had started to flow from the pipet, the latter was raised until the end of the stem was above the calibration mark on the flask. When viscous liquids were being measured, the flask filled very gradually and evenly, with no tendency to build up on one side. The time, in seconds, required for 10 ml. to drain from the viscometer was taken as the relative kinematic viscosity of the liquid.

Duplication of results proved to be very easy; variation between measurements were never greater than 1 per cent of the relative viscosity of the liquid being measured.

The flasks used for the measurements were washed several times with toluene, inverted, allowed to drain, and dried by warming in an oven. Toluene was also employed to clean the viscometer.

Standardization

The viscometer was standardized with water and glycerin at 20° C. and with glycerin at 100° C. Chemically pure glycerin having a specific gravity of 1.2611 at 25° C. was used for this purpose. These results are given below:

	Temperature ° C.	R.K.V. sec.
Glycerin	37.5	23.2
Glycerin	20.0	85.3
Water	20.0	1.8

INSTITUTE TURPENTINE TEST FOR GREASEPROOFNESS (23)

Apparatus

A piece of plate glass 8 inches wide and about 4 feet long is mounted horizontally over a mirror which is so tilted that the bottom of the plate glass can be seen conveniently in the mirror by an observer standing in front of it. Fluorescent lights are arranged to illuminate the bottom of the plate glass.

A suspension of du Pont Oil red dye in alcohol is prepared by grinding the two materials in a mortar. This suspension is brushed lightly over one side of a large sheet of cellophane to coat it lightly with the dye. After the alcohol has evaporated, the sheet is cut into 4-inch squares.

Blotter stock cut into 3-inch squares is also required in the testing method.

Flat weights slightly larger than the size of the blotter and weighing 170 grams are used to obtain good contact between the specimen and the blotter.

Testing Method

The specimen to be tested is cut to form a 4-inch square. Both creased and uncreased specimens are tested. Creased specimens are prepared according to the Institute method (22).

A square of the dye-coated cellophane is laid on the plate glass with the coated side up. The specimen is placed on the cellophane with the side up which is to be exposed to the turpentine. A piece of the blotter is laid symmetrically on the specimen, and turpentine is applied to the blotter with a pipet until the blotter is saturated. The weight is then applied to the blotter to effect good contact between the blotter and the specimen. The stop watch is started at the same time the weight is applied.

When the turpentine passes through the specimen and reaches the film of dye on the cellophane, the dye turns a bright red at the point of failure. The time required for the first failure, the number of failures at the end of 5 minutes, and the number after 30 minutes are recorded.

The test is carried out in an unconditioned room on unconditioned specimens. The average time for the first failure, the average number of spots at the end of 5 minutes, and the average number after 30 minutes are calculated. For development purposes, the average number of failures at 5 and 30 minutes is of considerable interest. If the number is the same or nearly the same at the end of 30 minutes as after 5 minutes, the failures are probably pinholes or mechanical defects in the coating or paper. If the number of spots is considerably greater at 30 minutes than at 5 minutes, the coating or paper is failing generally. In this manner, mechanical defects are distinguished from intrinsically poor greaseproof quality and the test is an aid in planning the course of the development work.

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