

EFFECTS OF FATS AND NONIONIC SURFACE-ACTIVE AGENTS ON STARCH PASTES¹

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ABSTRACT

Studies with a Brabender Amylograph showed that viscosity increased in a 6% corn starch paste at a progressively lower temperature as fat was added. The eleven natural and hydrogenated fats used, although varying widely in degree of unsaturation, showed substantially no differences in their effects on the gelatinization or the cooling curves of the starch paste.

Addition of surface-active agents to the starch-water-fat mixture usually resulted in a marked increase in the temperature at which viscosity increased, as well as in the shape of the cooling curve. These effects appeared to be related to the length of the hydrocarbon chain and the number of hydrocarbon chains in the molecule of the surface-active agent. The character of the hydrophilic portion of the molecule also exerted an effect.

Little information has been reported concerning the effects of fats on the cooking of starch. This is true, also, for surface-active agents of the types used in foods as emulsifying agents or bread softeners. The few studies published have indicated that fat has little or no effect on gelatinization (5,11,12). Investigations of the action of monoglycerides (12) and polyoxyethylene monostearate (2,4,5,6,9) have shown that both these surface-active agents inhibit the swelling of the starch granules and cause starch gels containing them to be soft and easily broken. In the present study the Brabender Amylograph was used to secure more complete information on the effects of substances of these types on starch gelatinization, as reflected by viscosity changes, and to demonstrate the relationships between their chemical structures and actions on the starch pastes.

Materials and Methods

The following fats and oils (Iodine Numbers in parentheses) were used in 6% corn starch pastes in amounts varying from 0.2 to 12% of the weight of the starch-water mixture: soybean oil (132) and five hydrogenated soybean oils (105, 93, 82, 69, and 38), corn oil (126) and two hydrogenated corn oils (99 and 59), cottonseed oil (109), and prime steam lard (62). Total volume of the mixture was kept at approximately 400 ml., since with larger volumes the fat was not dispersed adequately. Thus, the ratio of 24.0 g. (d.b.) of starch to 376.0 g. of water was retained, but the actual amounts used were decreased as

¹Manuscript received May 14, 1959. Contribution from the Department of Home Economics, University of Illinois, Urbana, Illinois. Presented at the 44th annual meeting, Washington, D. C., May 3-7, 1959.

amount of fat added was increased from 0.2 to 12.0% of the sum of the weights of the starch and water.

The oil or melted fat was blended thoroughly with the starch and the resulting mixture was slurried in the water, which contained sufficient sodium hydroxide to produce a pH value of approximately 6.5 in the paste after gelatinization. This method of mixing gave much better dispersion of the fat in the cooked paste than addition of melted fat to a starch-water slurry. The mixture was heated in a Brabender Amylograph from 50° to 95°C., held at 95°C. for 15 minutes, then cooled to 30°C. and reheated to 95°C. For determination of gel strength with the Corn Industries Gelometer, a similar mixture was poured after the 15-minute holding period at 95°C. into the gelometer testing jars, and the disks were embedded. Samples were stored at approximately 2°C. for 18 hours, then allowed to stand at room temperature for 15 minutes to minimize effects of temperature change on gel strength, and the test was made.

For tests of the effects of surface-active agents on starch pastes, the basic mixture was a 6.5% corn starch paste to which soybean oil was added in an amount equal to 6% of the weight of the starch-water mixture. Sufficient sodium hydroxide was used to produce a pH value of approximately 6.5 in the paste after gelatinization. When a surface-active agent was used, it was substituted for 6% of the oil in the basic mixture (i.e., its weight was 0.36% that of the starch-water mixture), and the weight of oil was reduced by the same amount. The surface-active agent was dispersed in the oil. As in the studies of the effect of fats and oils alone, the oil mixture was then blended thoroughly with the starch and the resulting mixture slurried in the water. The slurry was heated in the amylograph from 50° to 96°C., held at 96°C. for 15 minutes, cooled to 30°C., reheated to 96°C., and recooled to 30°C. Gels were prepared from similar samples held at 96°C. for 15 minutes.

At least two preparations of each combination of ingredients were pasted, one for complete record of viscosity changes and the other for gel strength determination. In most cases the viscosity values at comparable pasting times agreed within 10 Brabender units (B.u.) and the temperatures at maximum viscosity within 1.0°C. In the few cases where agreement was not within 20 B. u. (the reported reproducibility of the instrument (3)), or 2.0°C., several additional samples were pasted, all of which produced results agreeing, within the limitations of the instrument, with one of the original values.

Results and Discussion

The effects of additions of increasing amounts of soybean oil to a

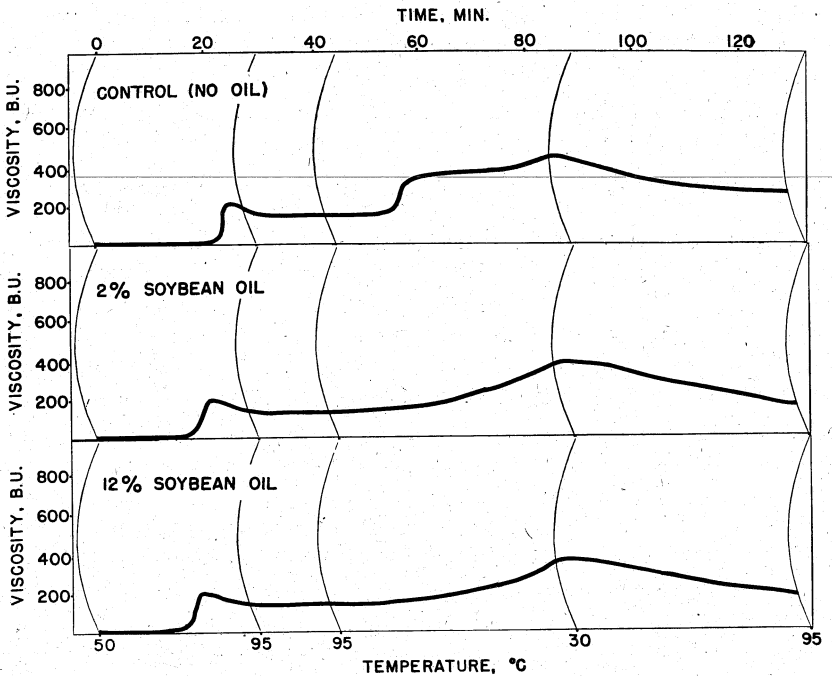


Fig. 1. Effects of soybean oil on amylograph curves of 6% corn starch pastes.

corn starch paste are demonstrated by the curves in Fig. 1. The addition of oil had no appreciable effect on the maximum value for hot-paste viscosity during the first heating. However, it appeared to lower slightly the temperature at which the initial increase in apparent viscosity was recorded, and it had a marked effect on the temperature at which maximum viscosity was reached.

As Anker and Geddes (1) have pointed out, the initial increase in viscosity is so gradual that the error in estimating the exact temperature at which it occurs, which they termed "temperature of transition," tends to be much higher than that involved in estimating the temperature at maximum viscosity. The temperature at the initial increase in viscosity lacks the significance of the gelatinization temperature, at which the starch granules lose their birefringence. Therefore, since the temperature at maximum viscosity appeared to have greater practical importance, as well as being subject to more accurate determination, it was the value chosen for making comparisons of the systems studied (Table I).

The effect of soybean oil in lowering the temperature at maximum viscosity became progressively greater as the amount was in-

TABLE I
EFFECT OF CONCENTRATION OF SOYBEAN OIL
ON TEMPERATURE AT MAXIMUM VISCOSITY

CONCENTRATION, AS PERCENT BY WEIGHT OF 6% STARCH PASTE	TEMPERATURE AT MAXIMUM VISCOSITY
	°C
0.0	92
0.2	90
0.5	90
1.0	88
2.0	87
4.0	85
6.0	84
9.0	82
12.0	82

creased, until the weight of oil equaled 9 to 12% that of the starch-water mixture. Larger amounts of oil seemed to have little additional effect, probably because no more oil could be well dispersed in the mixture. In addition to lowering the temperature of maximum hot-paste viscosity, the oil removed the characteristic step found in the cooling curve of the corn starch control paste (Fig. 1). Even 0.2% soybean oil completely eliminated this step. The presence of the oil lowered the viscosity attained when the paste was cooled in the amylograph to 30°C., and also after it had been reheated to 95°C.

Gels prepared from samples removed after the 15-minute holding period at 95°C. did not appear to differ substantially from the control. The inconsistencies in gel strength values observed may have been partially the result of the inhomogeneity of the pastes.

Neither degree of saturation nor source of the fat appeared to make any difference in its effect on the starch paste except in the case of pastes containing the most saturated fat, hydrogenated soybean oil with an iodine value of 38. Pastes containing this fat, when cooled to 30°C., had lower viscosities than the other pastes at this temperature. This effect was possibly associated with the fact that the fat particles solidified. At room temperature this fat was very hard and brittle.

In marked contrast to the similarity of the various fats and oils in their effects on the amylograph curves were the wide variations in effects obtained with various nonionic surface-active agents. The compounds listed in Table II were substituted for part of the fat in a starch paste containing soybean oil. Use of a mixture of surface-active agent in oil rather than the surface-active agent alone appeared to have several distinct advantages:

1. The combination formed a system similar to that found in foods, in which fat is nearly always present when a surface-active agent is used.

2. Several surface-active agents, when used without fat or oil, raised the temperature of maximum viscosity to such an extent that it was not reached even when the final temperature was raised from 95° to 96°C. and the mixture was held at 96°C. for several minutes. As a result, the shapes of the cooling curves of the pastes were greatly influenced by whether or not maximum viscosity had been reached, as well as by other effects of the surface-active agents. By taking advantage of the effect of oil in lowering the temperature of maximum viscosity, and by heating the mixture to 96°C., a peak viscosity was reached during the heating cycle with all but one of the mixtures studied. The cooling curves of the resulting pastes showed characteristics which appeared to be related to the structures of the surface-active agents present.
3. Fat-containing pastes permitted a better comparison of the relative effects of the various surface-active agents on temperature at maximum viscosity, because of the range between the temperature at the peak viscosity for the control, 81°C., and the top of the heating cycle, 96°C.
4. When fat was not used, larger amounts of surface-active agents

TABLE II
EFFECT OF SURFACE-ACTIVE AGENTS ON STARCH PASTES CONTAINING FAT

ESTER	TEMPERATURE AT MAXIMUM VISCOSITY	GEL STRENGTH
	°C	<i>g.-cm.</i>
Glyceryl monopalmitate	94	186
Glyceryl monostearate	96	150
Methyl alpha-D-glucoside-6-laurate	75	105
Methyl alpha-D-glucoside-6-palmitate	88	78
Methyl alpha-D-glucoside-6-stearate	92	73
3-Palmitoyl-D-glucose	92	...
3-Stearoyl-D-glucose	1/2 minute at 96	62
Ascorbyl palmitate	96	123
Sorbitan monostearate	94	132
Sucrose monostearate	2 minutes at 96	91
Polyoxyethylene monostearate (MYRJ 45)	1 minute at 96	43
Polyoxyethylene monostearate (MYRJ 52)	no maximum	18
Sucrose dipalmitate	84	59
Sucrose distearate	90	58
Sucrose ester (Seqol 260)	87	84
Polyoxyethylene sorbitan monooleate	91	130
Polyoxyethylene sorbitan monostearate	92	118
Methyl glucoside distearate	89	85
Methyl glucoside tallow emulsifier No. 2210	90	105
Methyl glucoside tallow emulsifier No. 2275	90	107
Lecithin	77	443
Sorbitan tetrastearate	84	379
None (6.5% starch paste with 6% soybean oil)	81	608

appeared necessary to produce noticeable effects. In the quantities used, some of them caused foaming of the mixture or caking of the surface-active agent on the cooling coil. These difficulties were not encountered in the fat-containing systems used.

The magnitude of the maximum viscosity reached during heating remained substantially unchanged, but the temperature at which it occurred was influenced by the presence of surface-active agents, as might be predicted from published results on the effects of some of these compounds on the swelling of starch granules (2,5,12). The length and number of fatty acid residues, as well as the nature of the hydrophilic moiety in the molecule appeared to affect this phenomenon (Table II).

The temperature at which maximum viscosity occurred with monoesters was higher the longer the hydrocarbon chain. With glyceryl monostearate it was 96°C., and with glyceryl monopalmitate, 94°C. Methyl alpha-D-glucoside-6-palmitate did not raise the temperature as much as methyl alpha-D-glucoside-6-stearate; the corresponding laurate, instead of raising it, lowered it below that of the control paste. Likewise, 3-palmitoyl-D-glucose did not raise the temperature as much as 3-stearoyl-D-glucose. A similar relationship appeared to prevail with compounds containing more than one fatty acid residue; for example, sucrose distearate raised the temperature of maximum viscosity more than sucrose dipalmitate.

An increase in the number of fatty acid groups from one to two lowered the temperature at maximum viscosity in the case of the stearates of both sucrose and methyl alpha-D-glucoside. However, in neither case was the diester preparation a single chemical compound and this effect, therefore, must be viewed with reservation.

Comparison of the various monostearates and also of the monopalmitates indicated that the nature of the hydrophilic portion of the molecule had a decided effect on the temperature of maximum viscosity, but the number of compounds studied was too small to give an indication of the factors involved.

The shapes of the cooling curves obtained when various surface-active agents were used showed great differences. Most of the monoesters (Fig. 2) produced cooling curves with a peak at about 70°C., although the temperature varied somewhat from one ester to another. These peaks were repeated in a second cooling curve after the mixture had been heated a second time. They may be related to the characteristic step in the cooling curve of ordinary corn starch. The step could be removed from the curve of corn starch by "defatting" through alcohol extraction, as previous investigators (10) had observed, as well

as by addition of oil, as discussed above. Although it has been stated that the curve of defatted starch can be returned to its original form by addition of "lipid" materials (10), it appeared that not all lipids have this effect. Glyceryl monostearate in very small amounts (0.5%

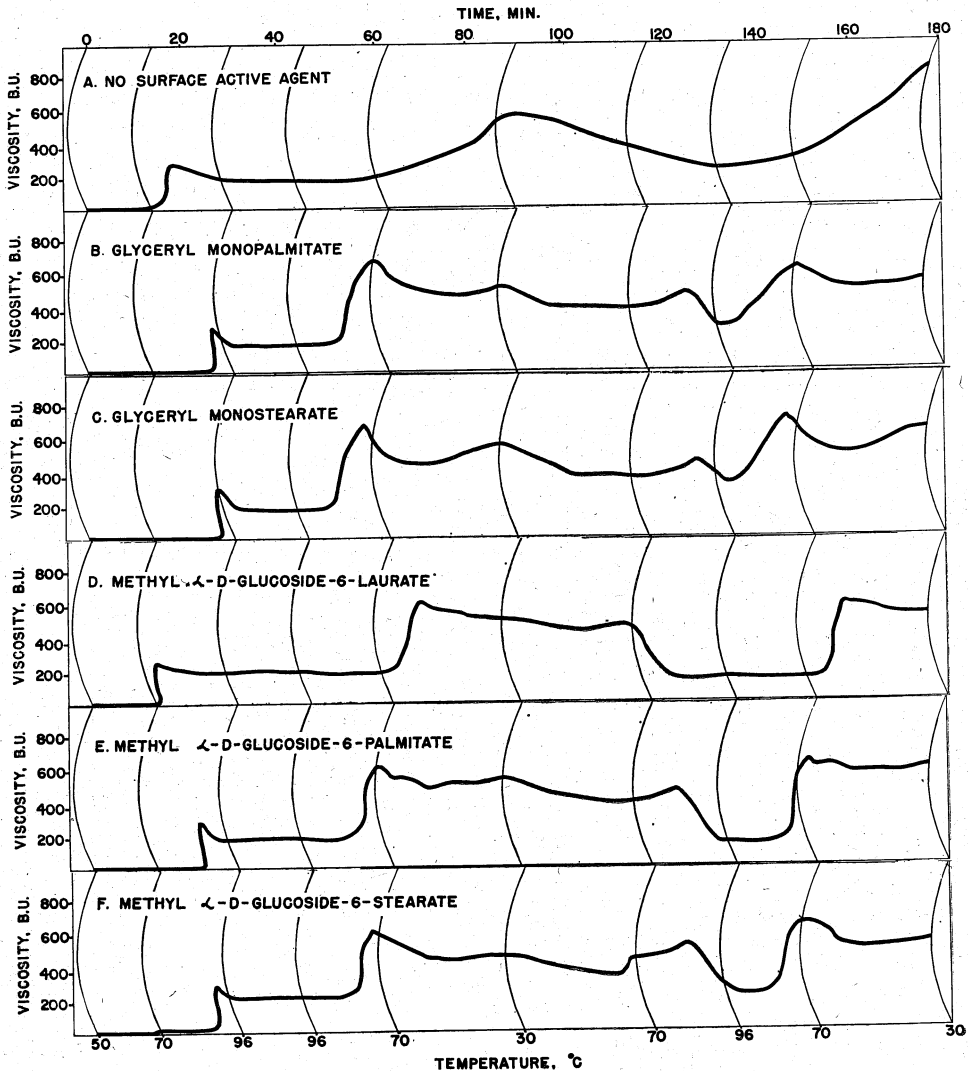


Fig. 2. Effects of 0.36% monosubstituted surface-active agents on amylograph curves of 6.5% corn starch pastes containing 5.64% soybean oil.

of defatted starch, but soybean oil and also lecithin were without any of the weight of the starch) introduced a peak into the cooling curve

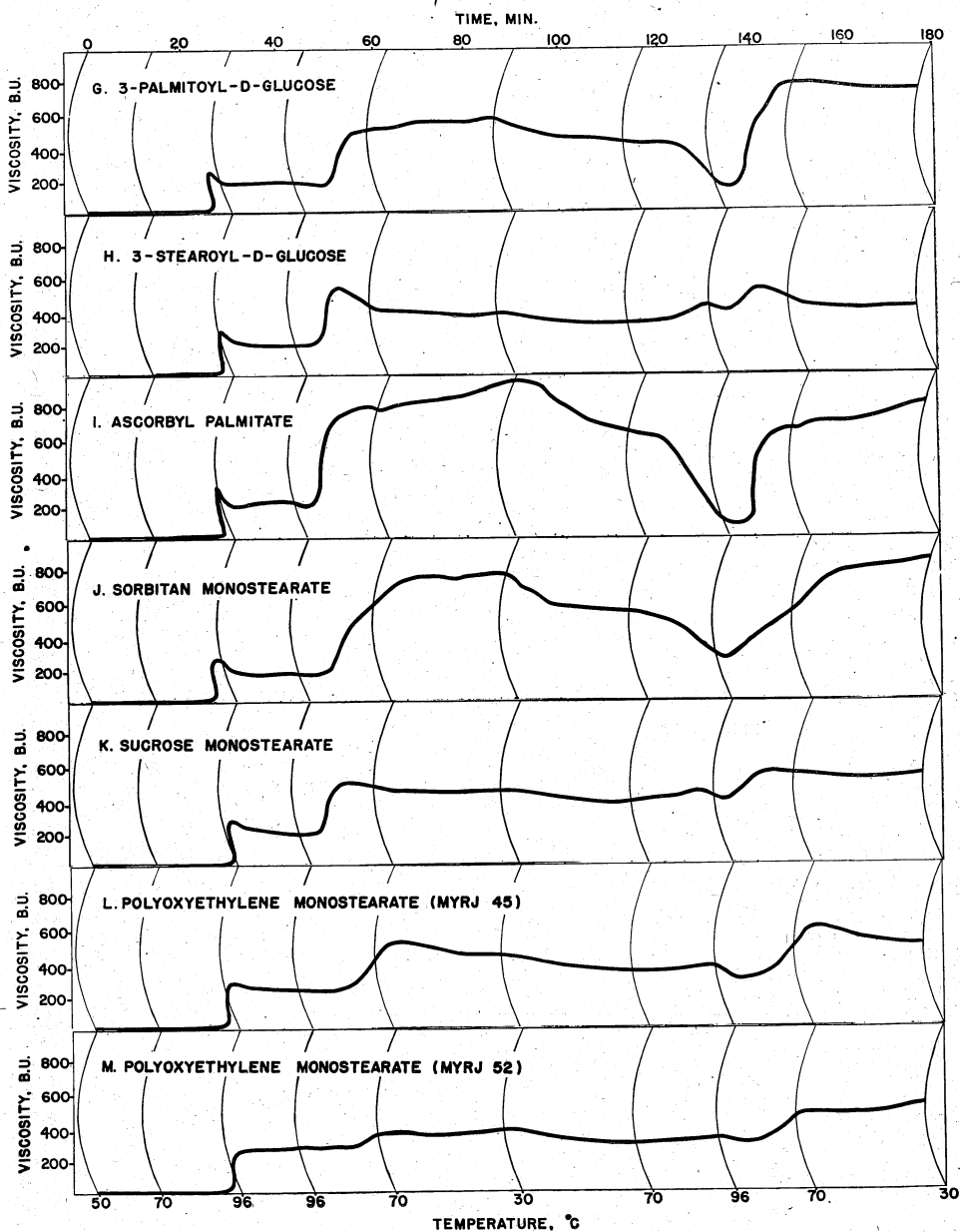


Fig. 2 (continuation).

effect. In agreement with previous observations (10), no such effects were observed with waxy corn starch. Thus it appeared that the amylose fraction and a substance with action similar to that of certain surface-active materials are needed to produce a step or peak in this portion of the curve.

The only polysubstituted substances which gave any indication of a peak in the cooling curves (Fig. 3) were heterogeneous preparations, a sucrose ester (Seqol 260) and two methyl glucoside tallow emulsifiers, which probably contained some monoesters. The corresponding diesters, sucrose distearate and methyl glucoside distearate, showed no peaks.

A few monoesters failed to show peaks in the cooling curves (Fig.

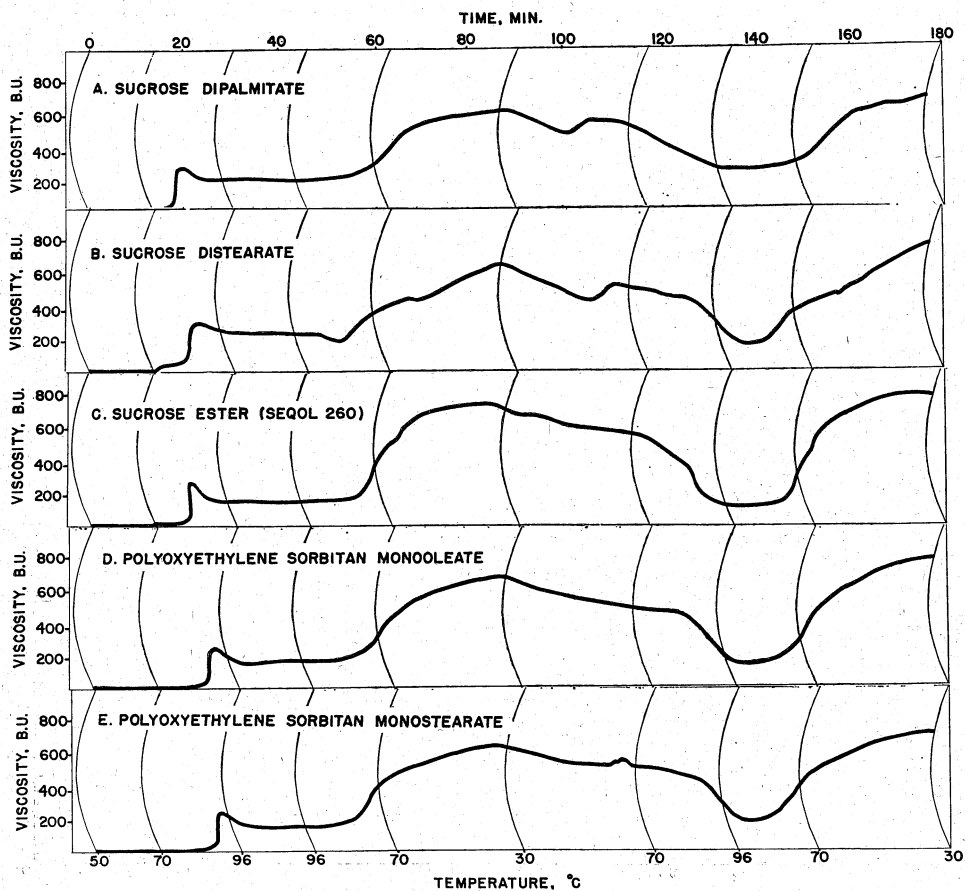


Fig. 3. Effects of 0.36% polysubstituted surface-active agents on amylograph curves of 6.5% corn starch pastes containing 5.64% soybean oil.

2). With polyoxyethylene monostearate (MYRJ 52) the fact that the compound inhibited gelatinization to such an extent that a peak was not obtained in the heating cycle was probably the cause. Ascorbyl palmitate required the addition of a large amount of sodium hydroxide to the mixture in order that the cooked paste should have the standard pH value of 6.5 used in this study. Thus the character of the compound was changed from that of the nonionic surface-active agents. In fact, the curve showed certain characteristics which were also found when sodium lauryl sulfate was substituted in the same system.

There appeared to be no obvious explanation for the lack of any definite peak in the cooling curves from 3-palmitoyl-D-glucose and

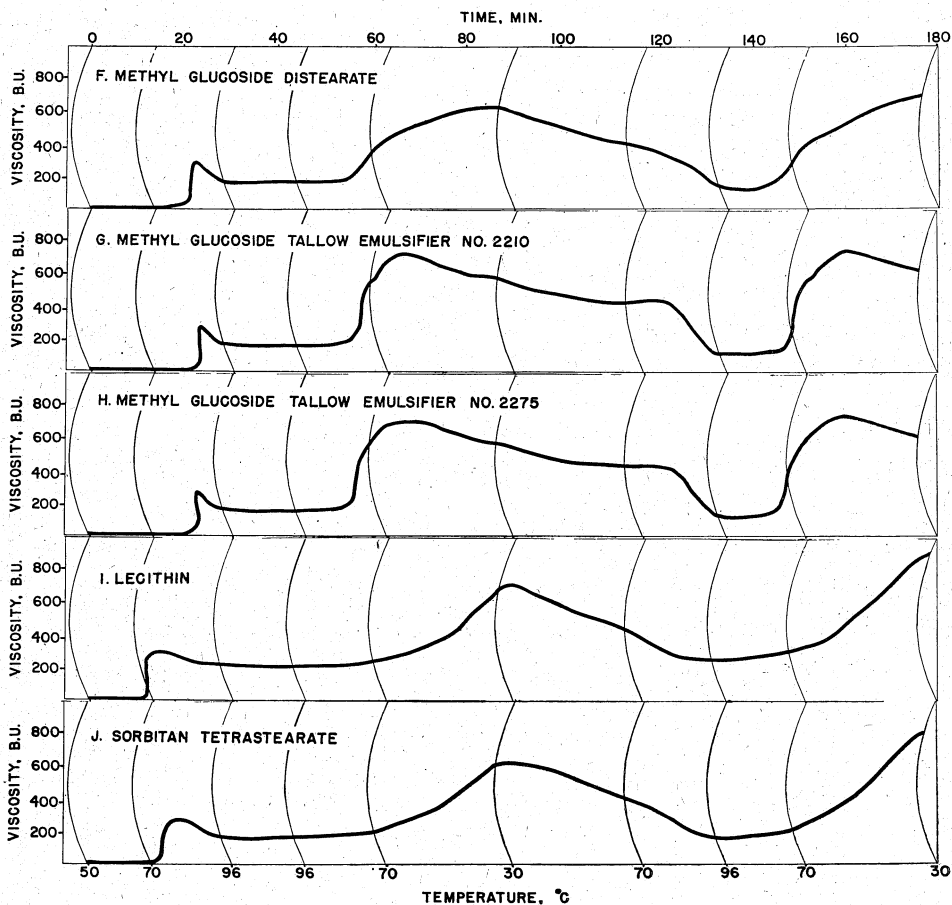


Fig. 3 (continuation).

sorbitan monostearate. However, the difference between the cooling curves of 3-palmitoyl-D-glucose and 3-stearoyl-D-glucose was somewhat comparable to the difference which has been reported for their actions as bread softeners (7,8). Although 3-stearoyl-D-glucose was judged to have excellent properties as a bread softener, 3-palmitoyl-D-glucose seemed to be almost completely lacking in such action.

All the polyesters but lecithin and sorbitan tetrastearate had pronounced effects on the shapes of the cooling curves (Fig. 3), generally causing a step to appear, but none gave rise to the peak found with most of the monoesters. Polyoxyethylene sorbitan monooleate and monostearate also produced large steps but not peaks. Although the curves with lecithin and sorbitan tetrastearate were similar to the control in shape, they were not identical with it. It thus appeared that there was some interaction between starch and all of these compounds different from that with fat alone.

Gels prepared from pastes containing any of the surface-active agents were much weaker than the control (Table II), although the effects with lecithin and sorbitan tetrastearate were much less than with the other additives tested.

Acknowledgments

The authors wish to thank the Corn Industries Research Foundation for a grant for support of this study. They also wish to express their gratitude to the following donors of materials used in the study: Swift & Co., A. E. Staley Manufacturing Co., Corn Products Co., Atlas Powder Co., Distillation Products Industries, Herstein Laboratories, Chas. Pfizer & Co., Inc., and U.S. Department of Agriculture, Northern Utilization Research and Development Division.

Literature Cited

1. ANKER, C. A., and GEDDES, W. F. Gelatinization studies upon wheat and other starches with the amylograph. *Cereal Chem.* **21**: 335-360 (1944).
2. BICE, C. W. A study of certain biochemical changes occurring in bread during staling. Ph.D. thesis, University of Minnesota, 1950.
3. BROWN, R. O., and HARREL, C. G. The use of the amylograph in the cereal laboratory. *Cereal Chem.* **21**: 360-369 (1944).
4. FAVOR, H. H., and JOHNSTON, N. F. Effect of polyoxyethylene stearate on the crumb softness of bread. *Cereal Chem.* **24**: 346-355 (1947).
5. LORD, D. D. The action of polyoxyethylene monostearate upon starch with reference to its softening action in bread. *J. Colloid Sci.* **5**: 360-375 (1950).
6. MARNETT, L. F., and SELMAN, R. W. Studies of the effects of polyoxyethylene monostearate on flour amylase activity. *Cereal Chem.* **27**: 349-358 (1950).
7. OFELT, C. W., MEHLTRETTER, C. L., MACMASTERS, MAJEL M., OTEY, F. H., and SENTI, F. R. Effect on crumb softness. II. Action of additives in relation to their chemical structure. *Cereal Chem.* **35**: 142-145 (1958).
8. OTEY, F. H., and MEHLTRETTER, C. L. Preparation of 3-stearoyl-D-glucose—a bread softening agent. *J. Am. Oil Chemists' Soc.* **35**: 455-457 (1958).
9. SCHOCH, T. J. The starch fractions. In *Starch and its derivatives*, ed. by J. A. Radley; 3rd ed., vol. 1, pp. 123-200. Chapman & Hall: London (1953); Wiley: New York (1954).
10. SCHOCH, T. J., and ELDER, A. L. Starches in the food industry. In *Uses of sugars and other carbohydrates in the food industry. Advances in Chemistry Series*, Vol. 12, pp. 21-34. American Chemical Society: Washington, D. C. (1955).

11. SCHOCH, T. J., and FRENCH, D. Studies on bread staling. I. The role of starch. *Cereal Chem.* **24**: 231-249 (1947).
12. STRANDINE, E. J., CARLIN, G. T., WERNER, G. A., and HOPPER, R. P. Effect of monoglycerides on starch, flour, and bread: a microscopic and chemical study. *Cereal Chem.* **28**: 449-462 (1951).

