

structure to the more ordered structure of the stable crystal is often slow. Crystals formed in natural fats frequently contain disparate molecules. The rate at which conversion to the stable polymorph occurs in such fats is related to mobility within the crystal structure. Mobility is associated with the plastic properties of the fat itself and, in the presence of liquid fat, with the solubility of the solid fat. Addition of liquid fat, such as olive oil or CBF-LM, to CB or CBF reduced the number of stable polymorphs in the mixtures due to the ease of conversion to more stable forms. Addition of liquid fat to CB and to CBF simplified the polymorphic behavior of these mixtures, and conversion to the stable crystal progressed more rapidly. Less energy was required for melting, as was evident on comparison of the peak area of CB of CBF to those of their mixtures with liquid fat. With the addition of liquid fat, the peak areas decreased to below that expected for the proportion of liquid fat present in the mixtures.

CB converted very slowly to the stable polymorph. Addition of 10% olive oil to CB markedly affected the rate of conversion and reduced the number of polymorphs present from the six found in CB alone to three in the mixture. On standing overnight at room temperature (ca. 22 C), CB containing 10% olive oil converted essentially to the highest polymorph. Stepwise tempering of this mixture was not favorable to conversion, producing only a small amount of conversion. Addition of 16.5% CBF-LM had much less effect on the conversion rate but expanded the melting range more than did the addition of 10% olive oil. There was no reduction in the number of identifiable polymorphs when the CBF-LM was added, but no more than four polymorphs could be identified when 10% olive oil was added.

CBF converted slowly to the stable polymorph. The endothermic and exothermic changes required considerably more energy than they did for either the CB or any of the various mixtures containing liquid fat. CBF behaved in a polymorphically complex manner, exhibiting five polymorphs. Addition of liquid fat (olive oil) simplified the polymorphic behavior; on adding 10% olive oil, the number of polymorphs was reduced from five to three, and 20% olive oil further reduced the number to two. Various amounts of olive oil added to CBF reduced the energy required for the endothermic and exothermic changes below that expected for the proportions present in the composition of the mixtures.

It is to be expected that addition of similar amounts of CBF-LM or of olive oil to CB would affect the polymorphic characteristics of CB to different degrees. CBF-LM had an iodine value of ca. 56 and a saturated fatty acid content of ca. 46%. The fraction was primarily liquid at room temperature (22-24 C) but contained a small amount of crystallized

fat. Also, some TGs in CBF-LM so closely resemble TGs in CBF that mixed crystal formation with the latter would be expected. Olive oil, on the other hand, has an iodine value of ca. 77, a saturated fatty acid content of ca. 19%, an oleic acid content of ca. 72%, and is completely liquid at room temperature. The TG composition of olive oil is such that the addition of a given amount to CB could provide greater mobility of the molecules within the crystal structure than that provided by addition of an equal amount of CBF-LM.

In several of the heating curves of well tempered samples, the heat of fusion was smaller than that of the corresponding sample when less well tempered. This phenomenon was found only in samples that had been tempered over a long period of time, usually having been stored at room temperature. For example, the area under Curve E, Figure 2 (90% CB-10% olive oil), is smaller than that under Curve D; and the area under Curve F, Figure 2 (83.5% CB-16.5% CBF-LM), is smaller than the area under Curve E. In Figure 3, Curve F (70% CBF-30% olive oil) and Curve D (50% CBF-50% olive oil) are further examples of a decrease in heat of fusion on extensive tempering.

These observations can be explained by mixed crystal formation. Rapid solidification of the fat mixture from the melt resulted in formation of a relatively homogenous solid in which normally liquid fat entered the crystal matrix at a molecular level. After limited tempering, the entire mixture acted as a homogenous solid, and the sample melted as a single solid phase. Extensive tempering, however, destroyed the relatively homogenous solid. The higher melting TGs segregated into a smaller amount of higher melting solid phase, and the lower melting TGs coalesced and segregated into a phase liquid at or near room temperature. This was a slow process, although marked variations in room temperature accelerated the segregation. When such a sample was melted during a DSC scan, only the solid phase adsorbed appreciable energy during melting, resulting in a lower caloric absorption for the sample.

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## ERRATUM

### Moulton Actual Chairman of Fats and Oils Symposium

In the January issue of *JAOCS* (53:27), Associate

Editor G.C. Cavanagh was mistakenly credited with chairmanship of the New Processing of Fats and Oils Symposium presented at the 66th Annual Meeting in Dallas and published in part in that issue. In fact, the chairman of the symposium, to whom we extend our sincere apologies, was Karl J. Moulton of the Northern Regional Research Laboratory (ARS, USDA) in Peoria, IL.