NOTE ON "HARDENED" OILS.

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It is possibly a convenient time for calling the attention of analysts to the fact that in the immediate future they will be called upon to analyse certain new artificial fats, and, not improbably, to detect their presence as adulterants. For many years attempts have been made to convert into stearic acid the oleic acid which is produced in such large quantities as a by-product in the manufacture of "stearine" candles. The chemical reaction appears to be a simple one—the mere addition of hydrogen. This has at last been accomplished by making use of the catalytic action of platinum, palladium, or nickel. The same reaction which converts oleic acid into stearic acid also converts triolein into tristearin. Thus, for example, starting with olive oil, as the absorption of hydrogen proceeds, a turbid oil, then a liquid mess, then a soft fat, and finally a hard fat, is obtained. A similar change occurs with all oils containing glycerides of unsaturated acids. This rise in the melting-point is naturally accompanied by a decrease in the iodine value and refractive index. I obtained, amongst others, the following results with cottonseed oil, hardened with the help of a nickel catalyst (see p. 103).

Fats have been prepared in this way from cottonseed oil with iodine values as low as 5, and if desired the iodine value could doubtless be reduced to 0, and the melting-point raised to 60° to 70° C. Whilst it is too costly for commercial purposes to carry the saturation of the unsaturated glycerides to completion, it might be of value in the laboratory as an aid to determining the component glycerides in a pure oil. Not only the oils containing glycerides of oleic acid can be hardened, but also

those containing glycerides of linolic acid and linoleic acid (the drying oils), and even of such highly reduced acids as clupanodonic (in whale oil). Anyone who has seen a malodorous oil converted into a bland odourless tallow realises the commercial possibilities of the process. And when it is remembered that the process can be stopped when the iodine value reaches a desired number, the possibility becomes evident of the preparation of a fat with any required analytical figures.

	Original Oil.	Hardened Oils.		
Appearance	Clear liquid	Solid particles, floating in oil	Soft greasy solid	Brittle solid
Butyro-refractometer (corrected to 40° C.)	57.7	—	—	47.7
Fatty acids:				
Iodine value	110	94	55	22
Titer	34.7° C.	37.0° C.	42.5° C.	57.2° C.
Neutralisation value (mgrms. KOH)	197	196	196	192

The analyst is chiefly interested in the question of how these new fats are to be detected. It is doubtful if their most characteristic feature, the relatively high percentage of stearic glycerides which they contain, will be of much service. Until the manufacturer accomplishes the difficult process of completely removing the nickel, the detection of traces of this metal will be the simplest and most reliable test for hardened oils. Although the catalyst is very finely divided, the manufacturer can obtain a perfectly clear fat by careful filtration, and hence it is the nickel contained in the nickel soaps formed by the free fatty acids present that one has to detect. The following method is suggested: 50 grms. of the fat is heated in a flask with 20 c.c. hydrochloric acid, with continued vigorous shaking. The mixture is allowed to separate whilst hot, and part of the acid solution is evaporated to dryness, dissolved in a drop of water, and placed on a white tile. One drop of ammonium sulphide is added to this, and also to a drop of water for comparison. I have only tried this test on a few hardened oils, and in some cases with negative results. Dimethylglyoxime is a much more delicate test, but unfortunately Prall has found (Bömer, *Zeitsch. Untersuch. Nahr. Genussm.*, 1912, **24**, 104; and *ANALYST*, 1912, **37**, 452) that certain pure untreated oils give a red coloration. Hence further investigation is needed.

One of the most characteristic tests for fish oils—the bromide estimation—is quantitatively useless for these oils after hardening, as the percentage of ether-insoluble brominated glycerides is greatly reduced thereby. Not only are the analytical figures for the oils altered by this absorption of hydrogen, but also the traces of substances which often serve as a useful test for the particular oil in which they occur—e.g., in Halphen's reaction (Bömer, *loc. cit.*). It is a remarkable and valuable observation that phytosterol and cholesterol are not changed in this process (Bömer, *loc. cit.*).

The three fats exhibited were obtained from a clear cottonseed oil. They were hardened by hydrogen with the help of different catalysts, and gave the following figures :

Catalyst.	Percentage of Catalyst in Oil.	Character of Product.	Butyro-Refraction (corrected to 40° C.).	Melting-Point : °C.
Nickel	1.00	Hard	45.7	49
Platinum	0.10	Hard	47.8	46
Palladium	0.06	Brittle	45.5	52

The keeping properties of these hardened oils are remarkably good. The above have been prepared for nearly a year and a half, have often been exposed to damp air, and show no signs of rancidity. The free acidity (0.70 per cent. as oleic acid) has not appreciably changed.

Hardened oils give soaps which are good in colour, but lacking in lathering properties. It is unlikely that any objection will be raised to their admixture with other fats for soap-making. Their use in the preparation of edible fats is more open to question, and in the interests of public health certain investigations ought first to be made to show (1) that no harmful substances are produced by the chemical changes in the fatty glycerides and unsaponifiable matter ; (2) that a high percentage of tristearin does not render the fat indigestible ; (3) that traces of nickel, from 1 to 10 parts per million, are not harmful. There is perhaps little to be feared from objectionable substances in the hydrogen used, as the majority of such substances would poison the catalyst.