Notes On The Silver Benzoate Test

By M. F. LAURO

ADULTERATING olive oil with foreign oils is not always the prevalent malpractice. Often inferior grades of olive oil itself are worked up to mix with virgin or edible quality oil. The blending of several pressings of low acid oils is considered good legitimate practice; consequently very little if any virgin or first press oil finds its way to this market. The next large sources tapped are the high acid or commercial oils which are refined with alkali to remove the fatty acids. A third but reprehensible practice, one common in years when conditions are conducive, is to add to the commercial as well as edible quality oils, the refined, bleached and deodorized pulp oils. Of the latter, there are three classes; those extracted from the olive pomace with carbon bisulphide and known on the other side as sulphur oils and over here as olive oil foots, those extracted with the chloroethylenes or other halogenated solvents, and those dissolved out by naphtha. A comparatively insignificant amount used to be made by fermentation and boiling, employing no solvent.

It thus becomes important at times for the analyst to determine whether a given sample is pure pressed olive oil or made wholly or in part from extracted oil. The usual chemical analysis reveals little difference between the various kinds, especially in mixtures with pressed olive oil. The constants are practically alike. The tests used therefore are directed at finding the traces of solvent left in the recovered oils even after treatment.

In the early years of its application, the silver coin test for sulphur proved adequate to detect those oils that were extracted with carbon bisulphide. They constituted the chief class of extracted oils. The term olive oil foots no longer applies solely to them, having passed from a special to the general designation with the more frequent production of other solvent extracted kinds. The Beilstein or copper-wire flame test for halogens, the writer remembers taking from organic chemistry text and applying it for the first time toward the detection of halogenated solvents in olive oil. There is no special reaction for the naphtha extracted oils. Characteristic of such is the unsaponifiable matter, which is greater in amount than in foots of other description, contains less sterolic constituents and gives lower iodine value.

The silver benzoate test came in response to the need for a test more sensitive than the coin to detect sulphur compounds, for as time went on, tests that were quite definite in the beginning, began to fail as soon as refiners became more skillful in removing the last traces of solvent from the recovered oils.

Originally, the writer experimented with silver salts soluble in oil such as the oleates, palmitates and stearates, in connection with a thesis on metallic soaps. As they proved unsatisfactory, attention was directed then to the insoluble salts of organic acids. The notion was to expose a far greater surface to the oil by finely divided silver than one would achieve with a silver coin. After much trial, the silver salt of benzoic acid was selected because of its easy preparation as a fine, dry powder and its reactivity.

First suggested in the September, 1927, issue of "Oil and Fat Industries," the benzoate test was taken up by many industrial firms, merchants and enforcement officials, with what success it is difficult to say, since so far as the author knows, very little has appeared in print regarding its application. There is considerable evidence, however, of its extensive use, here and abroad.

Last year, a few rejections of alleged virgin oils on the ground that they contained sulphur oil have placed both the silver coin and the benzoate tests in issue. The claims made against their reliability in certain quarters as yet have not been backed by any substantial proof. Samples from authentic sources have not been produced nor has the matter been taken up in any serious way. Though not a party to an issue that has arisen through the judgment of other chemists, nevertheless the writer, as one responsible for the benzoate test, feels it incumbent to disclose the data in his possession all these years bearing on that test, with the hope that other users of the benzoate reaction will publish their findings and opinion.

Begun in August, 1926, these notes include in chronological order the various steps taken to improve the test then invented, the many samples analyzed and certain conclusions drawn. The sensitivity of the silver benzoates is determined by adding a pinch of the powder to samples of pressed olive oil containing decreasing amounts of bisulphide solvent and heating them to 160° C. At a dilution of 0.05 per cent CS_2, the benzoate still gives a deeply positive reaction, although the coin is negative and the nose can still detect the odor of solvent. As little as 0.01 per cent gives a black coloration with the benzoate. Applying the test to mixtures of sulphur oil and pressed olive oil, a definite discoloration appears at as low a content as 0.2 per cent sulphur oil. The coin fails to indicate at less than 10 per cent. In the November, 1927, issue of "Oil and Fat Industries," Dr. Louis Roeg, then chairman of the Society's Olive Oil Committee, stated that the benzoate test was definite to 1 per cent extracted olive oil and, in comparing it with the coin and Fachini acetic anhydride tests, advised its adoption.

Then follow experiments to define the conditions and limitations of the test. Attempts to find a suitable solvent or carrier of silver to the oil are abandoned as needless. There is the question of proper temperature; also whether to add the reagent at the start or after the oil is heated. The former procedure renders the test extremely sensitive. In the presence of the silver salt, heating to 180° C. causes all oils to darken, except the refined pressed oils. These of course contain no substances in solution derived from the original olives which furnish the nuclei for the precipitation or reduction of silver from the benzoate. Below

160° C. samples containing sulphur solvent darken in proportion to the amount present. The pressed oils remain unaffected. The test is finally standardized at 150° C. Even at this temperature, if benzoate is added at the start, some pressed oils are found to discolor slightly, making it possible to confuse the inexperienced analyst. To avoid such a possibility, the test is purposely restricted in its degree of sensitivity to that of the coin test by heating the oil first to 150 C. and then dropping a pinch of benzoate into the oil, shaking it in and then noting the result immediately. An appreciable discoloration as compared with the same oil heated without the silver salt, indicates the presence of sulphur extracted oil. Using this modification, a few hundred samples were tested and results compared with the coin and the Fachini methods. The Fachini test did not always give concordant results; often they were positive where negative was to be expected. Under the conditions of the modified test, the benzoate and the coin tests agree with no exceptions found. Hence this is the test that was recommended in 1931 for adoption by the Society, as insuring the maximum of safety in the interpretation of results. In doing so, however, the value of the silver benzoate test was depreciated considerably.

Other chemists have employed modifications in which the silver benzoate is added in the beginning to the oil to be tested and then heated to 150° or more. These different ways make the test much more sensitive than the official method. Unless carefully interpreted, false conclusions may be reached. The writer himself prefers to use the test at 99 C., in which 5 cc. of the oil to be examined with not more than 50 milligrams of the dry benzoate powder are shaken up in a test tube and placed in a boiling water-bath for five minutes. This, too, is a great deal more sensitive than the official, but, having tried it on many hundred samples, its reliability is established to his own personal satisfaction.

Continuing with the notes, we find the test employed to detect three classes of olive oil. The official method differentiates the sulphur extracted oils from the pressed oils. Carrying the heat to 180° C. in the presence of the benzoate serves to sort out virgin oils from the refined oils, in that the benzoate remains unaffected where there is no sulphur present until that temperature is reached, when the virgin oils discolor at once and the refined oils still yield a negative reaction. The test at 99° also show up refined oils by the fact that the color bleaches out to almost water-white.

Oils other than olive are tested with benzoate. Crude vegetable and animal oils give erratic results. The matter contained in crude oils introduce unknown factors. The silver changes some to orange, brick red and even black, and sometimes the characteristic silver mirror is produced on the sides of the test tube. These oils are therefore excluded from further examination, though very interesting colors are noted in the case of some oils like rape, sesame, teaseed and soya.

In the case of those other oils that are marketed as salad oils, namely, the finished, refined and deodorized oils, like sesame, cottonseed, rape, sunflower, etc., the benzoate tests are all negative. All the leading brands of olive oil are also negative. In the case of commercial oils, it was a relative easy matter to check up any positive benzoate reaction. The test was never doubtful, being either negative or so strongly positive that other tests could be used to confirm. There never was any complaint as to positive tests on these oils. But when it came to the so-called virgin oils, outside of those sold in cans ready for home use, exceptions begin to pop up. The writer noted five in 1928. These oils were bitter, unusually so, and as they stood, decidedly unfit for edible purposes. Their history is unknown. This led to collaborative work with a few merchants who were in a position to secure authentic samples. Each year since, the writer has been furnished by reputable dealers with samples of oil from California, Spain, France, Italy and Africa. His own relatives sent him oil from local presses in Italy for examination. His results checked with the data later supplied after the tests were completed. The evidentiary facts on which the reliability of the benzoate reaction is upheld, are based on a few thousand samples, at least one hundred of which are vouched for.

There are certain matters extraneous to oil but sometimes present, which may or may not affect silver benzoate. These are soap, iron, copper and coloring matter. The natural green olive oil that is used to mix with cotton and other oils, to produce the composite true olive color for making salad oil, gives a negative reaction, while olive oil that is artificially colored darkens with the benzoate. The presence of slight amounts of soap in a finished oil causes the benzoate to react positively. Olive oil containing copper in solution in certain instances give positive tests, though the test failed in those cases where the writer added copper stearate to the oil. A little free alkali has no effect. This is also true of free fatty acidity, though with excessive content, as 50 per cent or more there is a slight darkening, but then heat alone tends to produce the same result. Rancidity or age may affect results. The amount of benzoate added affects its sensitivity; the test is less reactive with greater amounts. 20 to 30 milligrams are sufficient, a mere pinch. Also, freshly prepared benzoate is found more reactive than when old or grayish. The salt, however, keeps well in amber bottles. When made, it should be white and not gray, and should be perfectly dry.

Because of the possibility of colloidal matter or fine suspension of substances accidentally present and of moisture, it is advisable to filter a sample to be tested, through a double layer of fine filter paper, even though the sample appears perfectly clear to the naked eye. To adjudge a test as positive, the darkening should be appreciable. There should be no question when the test is positive. It is only when a slight discoloration places the sample on the "fence" that a doubt arises and it is well to resolve it in favor of the oil, unless the presence of sulphur compounds can be confirmed by other tests, or something of its history is known. Flavor, odor on heating, appearance and color of the oil are factors to be considered.

The test is properly applied to olive oil only, though other oils of edible quality likely to be used as adulterants have been tested and found to give negative reactions. Sulphur may not be the only substance that will darken the silver, but in actual practice, other substances likely to affect it are either eliminated or just as improperly present. Soap is not a natural ingredient of olive oil; its presence would indicate refining. Copper and artificial coloring in edible olive oil are objectionable impurities. All may be accounted for by other tests, if a positive benzoate reaction is suspected as due to these. It is submitted that these exceptions do

not in the least detract from the value of the silver benzoate test.

The particular samples of last year's oil that have brought up the question at issue were intensely bitter oils. Those that the writer examined were too acrid to dismiss on the ground they were virgin oils and therefore naturally harsh. As a matter of fact the free fatty acidity was only 0.2 to 0.3 per cent, unusually low. Two to three whole per cent is the usual content in virgin or first press oil, according to the writer's experience. Of course these oils were never intended to be sold directly for table use, being destined for blending with other olive oils. Examination of two of them showed soap present, one revealed traces of copper, and the other two nothing to indicate the reason for a positive benzoate test if reliance is had on the seller's word that no sulphur compounds are present. Unfortunately, it is extremely difficult to make a chemical determination of the actual sulphur present in oils that have been mixed with extracted oils from which practically all traces of solvent have been steamed out. Other indirect tests like the Fachini, the Morawski and the Jaffé gave positive results on all these "exceptional" oils. The coin test was negative, however, in each case.

Two of the samples are from Seville, Spain, and the other three from Tunis. It has been argued that these harsh and bitter Andalusian and Tunisian virgin oils are exceptional in that they will give the positive benzoate test without having any content of sulphur compounds; at least that this is true of the 1934 crop. The Tunisian oils are admittedly exceptional in some respects such as iodine value from the general run of Italian and Spanish oils. Whether that makes them behave differently in the silver tests is something requiring proof.

A test rises or falls on the investigations following its discovery. The silver benzoate test has been in extensive use since 1927 without any published criticism all these years. This raises an almost conclusive presumption of reliability. It is still rebuttable, of course, but proof to the contrary would have to be of a substantial character to justify its reception. These relatively few exceptions have occurred so recently that the time has been too short to permit thorough investigation. Virgin oils always introduce controversial questions; the ultra-violet ray examination of such oils is a case in point. The very definition is subject for argument. These are not finished oils in the sense that they appear directly on the market. Rather are they used for blending. Some time must elapse before such oils "mellow" out and lose some of their "nascent" properties, which might conceivably throw the silver benzoate test. It is just as true of olive oil as of beverages that aging removes the harsh flavor. In the particular samples at issue, the harsh flavor still persists after many months, indicating something in solution which time does not efface. What is it? Is it sulphurous compound or traces of insecticide from the olives finding its way into the pressed oil? Or are such peculiarly bitter oils real exceptions?

The following data represents a condensed statement of the behavior of the silver benzoate test on olive and other edible (refined) oils:

Kind of Oil	FFA	Color	Reaction with Silver Benzoate: Color of the Oil	Decision
Sunflower	0.11%	20 Y — 2.0 R	Straw	Negative
	0.10	20 Y 1.7 R	Light straw	Negative
	0.10	9 Y 0.7 R	Light straw	Negative
Sesame	0.10	10 Y 1.0 R	Light straw	Negative
	0.10	8 Y 0.8 R	White	Negative
	0.08	3.5 Y 0.3 R	White	Negative
Soya Bean	0.05	30 Y 3.0 R	Straw	Negative
	0.10	20 Y 2.0 R	Light straw	Negative
	0.12	30 Y 2.8 R	Orange	Negative
Corn	0.30	Light yellow	Orange	Negative
	0.04	35 Y — 3.4 R	Yellow	Negative
	0.10	35 Y 3.0 R	Light yellow	Negative
Peanut	0.10	20 Y 2.0 R	White	Negative
	0.08	10 Y 1.0 R	White	Negative
Rapeseed	0.12	Light yellow	Light yellow	Negative
	0.08	Light yellow	Orange	Negative
	0.10	Almost white	White	Negative
Teaseed	0.08	Light yellow	Orange	Negative
	0.12	Light yellow	White	Negative
Cottonseed—PSY	0.08	35 Y — 6.0 R	Straw	Negative
Salad	0.03	35 Y 6.0 R	Light yellow	Negative
Winter	0.05	20 Y 2.2 R	White	Negative
Lard Oil	0.35	Light yellow	White	Negative
	0.50	Light yellow	White	Negative
	1.00	Yellow	Light yellow	Negative
Olive: Virgin	2.50	Golden yellow	Yellow	Negative
Commercial	4.90	Greenish yellow	Yellow	Negative
Usual edible	0.48	Golden yellow	Yellow to orange	Negative
Titer fatty acids		Smoky yellow	Dark yellow	Negative
Soap fatty acids		Yellow to green	Light yellow	Negative
Rancid and old		Almost white	White	Negative
Refined edible	0.18	Light yellow	White	Negative
CS_2 extracted		Smoky yellow to reddish yellow	Reddish brown to black	POSITIVE