

cacy with the more common ones using chemical reagents. It certainly fails long before the bitter taste disappears.

From the table it would seem that  $MnO_2$  should be given the first rank, but the slowness of its action is greatly in its disfavor, and the consequent difficulty of getting the color to flow down the side of the dish from the crystal of reagent is an objection. The presence of a little organic matter, also masks its action.

Altogether, we found that  $K_2Mn_2O_8$  gave the most satisfactory results. Of course, the color of this reagent is an argument against its use, but if the acid used be of full concentration, and if a blank experiment be run at the same time with acid only in the dish, no trouble need be feared from that source.

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## THE DETERMINATION OF MELTING-POINTS AND THE COMPOSITION OF SOME CANDLE MATERIAL.

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THE so-called melting-point of a fatty substance is obtained in such a variety of ways, and with equally varied results, that the claim of a certain figure for any particular article of commerce is really of little or no value, unless accompanied by a description of the method employed in its determination, which for ordinary trade conditions is hardly feasible.

There is probably no method in common use, even comparatively independent of personal equations and respective laboratory conditions. Those proposed for determining melting-points in capillary tubes etc., besides being open to these objections, necessitate allowing the fat to harden for many hours before applying the test. Wiley's method for butter fat is both tedious and difficult of manipulation and of course useless for free fatty acids.

The solidifying point, after Dalican, is not infrequently reported as the melting-point of stearic acid candles, and would if this were the only material employed, be an easy and fairly good solution of the problem; obviously, however, it is valueless for paraffin-wax and even for many mixtures of the two. The writer believes that any procedure which will quickly give

results on all kinds of candle material, the figures capable of being checked by different manipulators, is a much felt want among chemists engaged in such work.

In American oil refineries the melting-point of paraffin is usually determined by immersing the bulb of the thermometer to two-thirds its length in the molten wax, which is then permitted to cool slowly until the first signs of incipient solidification appear on the surface, disregarding that portion in immediate contact with the sides of the dish. The height of the mercury is then read off.

In some works this is slightly varied by drawing the point of a pin across the surface of the melted wax, until a "string" of the latter can be picked up. This is regarded as the melting-point.

A modification of Dalican's method, seemingly capable of universal application to substances solid at ordinary temperatures, was some time ago called to the writer's attention by Mr. Thomas S. Gladding. It consists of observing the temperature at which a fatty substance solidifies while in constant agitation.

The process is conducted by Mr. Gladding in the following manner: Thirty to fifty cc. of the dried sample is placed in a small beaker, the bulb of the thermometer is completely immersed therein and the glass with its contents twirled continuously in one direction until the mercury stops receding or ascending.

At first it falls rapidly and regularly but its subsequent behavior varies with the nature of the substance under examination. With fatty acids there is a rise of from  $0.1^{\circ}$  to  $1^{\circ}$  C., averaging about  $0.3^{\circ}$  for commercial stearic acid; here it remains stationary for about one minute. With paraffin-wax no rise results, but the mercury remains stationary about one-half minute and then continues to recede at the rate of  $0.1^{\circ}$  to  $0.2^{\circ}$  per minute. The fall prior to reaching this point being much swifter, no difficulty is experienced in noting the exact temperature. With mixtures of stearic acid and paraffin there is great diversity, the observed figures ranging from no rise, to one of nearly  $4^{\circ}$ . The latter representing a mixture of two-thirds stearic to one third wax.

Following is a table showing this melting-point of such mix-

tures in different proportions. The last column gives the action of the mercury at the time of solidification:

	Stearic.	Paraffin.	Melts at	
1.....	100	0	54.6	0.1 rise.
2.....	100	10	53.4	No "
3.....	100	20	52.4	" "
4.....	100	30	51.6	" "
5.....	100	40	50.8	0.05 "
6.....	100	50	50.1	0.2 "
7.....	100	60	49.2	0.6 "
8.....	100	70	48.2	0.8 "
9.....	100	80	47.4	2.8 "
10.....	100	90	45.6	0.6 "
11.....	100	100	45.2	0.8 "
12.....	90	100	45.8	No "
13.....	80	100	46.3	" "
14.....	70	100	46.9	" "
15.....	60	100	47.3	" "
16.....	50	100	47.9	" "
17.....	40	100	48.6	" "
18.....	30	100	48.9	" "
19.....	20	100	49.6	" "
20.....	10	100	50.4	" "
21.....	0	100	50.8	" "

To check No. 9, the same paraffin was mixed with another sample of stearic and gave:

	Stearic.	Paraffin.	Melts at	
	100	0	53.1	0.6 rise.
	100	20	50.8	0.6 "
	100	40	49.0	0.7 "
	100	60	46.5	3.6 "
	100	80	45.9	3.1 "

NOTE.—These tables were constructed with a view to practical uses, hence, the proportions, as above, instead of even percentages reckoned on the mixture. In candle factories the predominant material is taken as a basis of calculation. Thus, forty per cent paraffin means 100 parts stearic acid to forty parts wax.

The great advantage claimed for this method is the concordance of its results in different hands. The figures obtained are always the same to 0.1°. The only caution necessary is in cases where apparently no rise of the mercury will take place; the twirling motion should be continued until the mass assumes an unbroken white color and a homogeneous semi-solid consistency. This may take some minutes; then if still no rise occurs the temperature at which there was a pause

is to be noted. A few trials with a mixture like No. 9 will make this clear.

The thing to guard against is being deceived by an action of the mercury similar to say No. 15. For several minutes before the enormous rise in the former, it almost stops, sinking no faster than after reaching the true point in the latter. The appearance of the substance under examination is, however, vastly different, being in No. 9, coarse, white flakes floating in a clear molten liquid. On continuing the motion, the mass suddenly blends to a solid white, the temperature rising rapidly; the highest point reached being the melting-point. On paraffin-wax, the refinery test previously mentioned, shows about  $0.6^{\circ}$  C. higher than Gladding's.

Chemists have for some time been aware that a mixture of fatty acids, subjected to distillation with superheated steam, undergoes some change. It is known that a quantity of liquid hydrocarbons is formed, together with a black pitch; also that there is a slight increment in the melting-point. Alder Wright ascribes this latter to the possible formation of isoleic acid or stearolactone. A limited investigation by the writer, carried on at a large candle works, is felt to be a small grain added to a rather barren fund of literature on this subject.

An oft occurring mistake in connection with published analyses of candle material, is the omission of the details of manufacture. For instance, to give the average composition of commercial stearic acid, means absolutely nothing when we consider that one manufacturer employs palm-oil as a source while another uses tallow or bone-fat. A third both saponifies and distills with steam while a fourth uses sulphuric acid or presses the fatty acids directly without distillation. It therefore becomes essential to preface any report of this kind with a brief outline of the several stages through which the fatty substances pass.

The fats under consideration here are exclusively tallow and bone-fat. These are saponified in an autoclave under 150 pounds steam pressure and without the aid of any base. All that is of sufficiently good color is then at once subjected to pressure at ordinary temperature, followed by a second hydraulic pressing, at steam heat. The solid cake of fatty acids thus obtained,

needs only to be freed from dirt before being ready for the candle-molds. The oil expressed hot is permitted to chill, re-pressed cold, and the solid residue again subjected to the hot pressing. This is continuous, the cake from the hot press alone being used in the molding room.

The dark fatty acids, from the autoclave, before receiving the above treatment, are subjected to distillation, in copper, with superheated steam; 16,000 to 18,000 pounds constituting one "run," during which the volume in the still is kept constant by a continuous inflow from the storage tank above.

The distillate is caught in three fractions. The white oil, comprising about four-fifths of the whole is obtained first. This we will call "first run oil;" it is ready for pressing at once. The hydrocarbons that are formed having, in part at least, a higher boiling-point than the fatty acids, accumulate in the still and when these begin to come over in quantity sufficient to color the distillate a decided green, the receptacle is changed. What now comes over we will term "second run oil;" it is returned to the storage tank and redistilled with the next run.

After a time the distillate again changes color becoming darker and more viscid. The operation is then stopped and the contents of the still permitted to cool, subsequently being transferred to a smaller iron still in which a higher heat can be attained. The fraction obtained here we will designate "green oil." There now remains as a residue a black pitch, called "candle tar."

As will be seen later, from its analysis, the practice of returning this green oil to the storage tank, for redistillation with other fatty acids, can not be looked upon in any other light than as an adulteration of the red oils, finally obtained, into which it finds its way.

Going back to the autoclave we find little of interest except perhaps the degree of perfection attained by this mode of saponifying, without any base. Samples removed after ten, twelve, and fourteen hours digestion, showed respectively 1.74, 1.44, 1.06 per cent. glycerol.

NOTE.—The unsaponified fat may be approximately deduced on multiplying these figures by ten.

As might be expected, no change occurred in the constitution of the fat, other than the removal of glycerol. Facilities for trying the effect of higher pressure than 150 pounds were lacking.

Proceeding to the distillation, we find the following changes take place:

BEFORE DISTILLATION.		AFTER DISTILLATION.	
Melting-point.	Per cent. oleic acid. <sup>1</sup>	Melting-point.	Per cent. oleic acid.
41.5	43.96	44.5	35.06
43.6	44.64	45.5	36.06
43.9	41.67	45.0	34.00

These melting-points are lower than those of the pure fatty acids alone; due in the first column to the presence of neutral glycerides, to the extent of ten to fifteen per cent., and to hydrocarbons from a previous distillation, as before mentioned. Distillation almost eliminates the former, but the hydrocarbons are still there in about the same proportion (*vide infra*).

To determine quantitatively the changes wrought by the high temperature, about 260° C., a run of 16,075 pounds was traced through, and the chemical composition before and after noted, as well as the proportion of the different grades of oil previously named. These figures may be taken as typical, the variation from averages being very small.

The oil had a melting-point of 43.2° C. and contained:

	Before distillation, per cent.	After distillation, per cent.
Solid acids.....	49.52	50.47
Oleic acid.....	42.86	33.05
Hydrocarbons (liquid) .....	6.94	13.14
Glycerol <sup>2</sup> .....	1.37	....
Tar.....	....	2.00
Loss.....	....	1.34
	100.69	100.00

The percentage yield of the different grades of oil and the constitution of each was:

<sup>1</sup> NOTE.—All the percentages of oleic acid given in this paper were obtained by calculation from the iodine absorption figure. The melting-points are those described in the beginning of this article.

<sup>2</sup> NOTE.—One-half the glycerol found is subtracted, together with oleic acid and hydrocarbons, from 100 to determine the solid acids, since tallow glycerides yield approximately ninety-five per cent. fatty acids and ten per cent. glycerol.



soft enough to lower the melting-point of its associates—stearic and palmitic.

NOTE.—As shown by several writers, the lowering of the melting-point of a mixture of two fatty acids by the addition of a third, does not necessitate the latter having a melting-point below that of the two former.

Apart from the evidence already given its presence is indicated by its low molecular weight, being—probably considerably—under 268, while the mean of stearic and palmitic as occurring in tallow is 271–272. The following tabulated analyses of press-cakes in different stages of completion, illustrate these points.

	AUTOCLAVE STOCK.				STILL STOCK.			
	Melting-point, ° C.	Per cent. oleic acid.	Total mean equivalent.	Molecular weight of solid acids.	Per cent. oleic acid.	Total mean equivalent.	Molecular weight of solid acids.	
1....	51.0	....	....	....	16.69	....	....	
2....	51.5	21.08	....	....	....	....	....	
3....	53.6	....	....	....	7.02	....	....	
4....	53.8	11.57	....	....	....	....	....	
5....	54.1	9.00	....	....	....	....	....	
6....	54.3	....	....	....	6.51	269.2	268.3	
7....	54.4	8.40	....	....	5.51	269.2	268.4	
8....	54.5	....	....	....	5.96	268.4	267.5	
9....	54.6	....	....	....	6.00	268.0	267.0	
10....	54.8	....	....	....	4.99	268.4	267.6	
11....	54.9	6.60	272.0	271.2	4.16	270.0	268.4	
12....	55.5	4.37	....	....	....	....	....	
13....	55.6	4.02	272.0	271.5	....	....	....	
14....	56.0	3.74	272.8	272.4	....	....	....	
15....	56.1	3.96	272.0	271.5	....	....	....	
16....	56.2	3.03	....	....	....	....	....	

NOTE.—The average content of neutral glycerides was determined to be 3.90 per cent. in samples 11, 13, 14, 15, from the autoclave, which is offset by an average of 0.17 per cent. hydrocarbons in samples 6 to 11, inclusive, from the still. In calculating the mean equivalents, no corrections were made for these in either case. The method of determination was; boiling with an excess of alcoholic potash and back titrating.

To sum up, in conclusion, it appears that when oleic acid is distilled in an atmosphere of steam, the distillate contains, besides unaltered oleic acid, hydrocarbons—liquid, and mainly of high boiling-point—and one or more fatty acids, not isomerides of oleic, having a considerably higher melting-point and lower mean equivalent than the latter, and differing therefrom in not forming addition products with iodine. A black pitch remains as a residue in the still.