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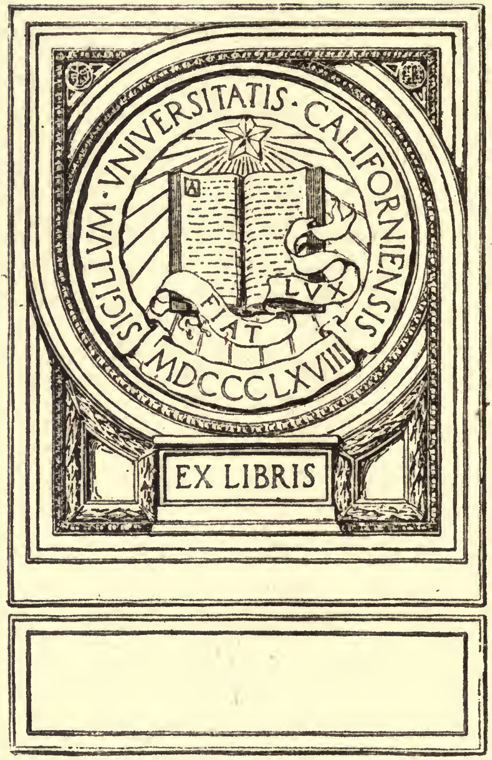
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1917.

PREFACE.

The following methods are given as works methods, and it must be clearly understood that the chemical methods used in the analysis of oils and fats can, from their nature, have no pretence to a degree of accuracy such as is usually found in inorganic work. The majority of the processes used in the analysis of oils are dependent on the use of solvents, and consequently the result obtained varies with the season of the year and many other factors. There has been a great tendency of late years towards building up theoretical foundations for the various methods used, and yet in commercial work products are obtained which cannot be made to yield concordant results in duplicate estimations, and also, as will be seen from the results given later, some of the processes which are supposed to be on settled bases give results which are quite inexplicable on the current theories.

All the figures given are now published for the first time. I have not entered into theoretical discussions for the reasons given above, and it appears to me that workers are much needed who will consider their results without attempting to bind themselves to preconceived notions.

G. F. PICKERING.

Horsforth, near Leeds,
July 1917.

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OILS AND FATS.

SECTION I.

SAMPLING, AND PREPARATION FOR ANALYSIS.

Sampling.—This must always be done with the greatest care; bad sampling has caused more differences by far between buyer and seller than the use of different methods of analysis.

The samples in the oil trade vary from thin fluids through semi-solids to solids so hard that in some cases the tester used for sampling has to be warmed, so that complete samples through the package may be obtained.

When sampling large lots, it is usually sufficient if every third package be sampled, all the samples put into a clean, dry bucket, the contents of the bucket well mixed, and four six-ounce bottles filled from the bucket, and sealed up at once; this allows one sample for the buyer, one for the seller, and one to be kept by each in case of dispute.

If a parcel is found to be dirty, or to contain more than a normal amount of water, it will be necessary to sample every package, and mix and seal the samples as before.

Solid Fats.—When the package is not full to the top, a sample bored right through the contents with an auger will fairly represent the contents of the package. Should free water be found, it is best to make a small hole at the bottom of the head, and allow the water to run out, and reweigh the package before sampling. Should the contents be up to the bung hole, it shows that the package had been stood on its head before the contents solidified after filling; cases have been known where this has been done in order to make accurate sampling very difficult, but this may be overcome by taking out the head, which was at the bottom when the package was filled, and boring a sample from end to end of the package; the difference in sound on striking the heads at once indicates the full end.

Liquids and Semi-Liquids.—These cannot be properly sampled with a tube open at both ends. Samples must always be taken with a closed slide tester, the tester being pushed to the bottom of the package before opening the slide, and the slide again closed before withdrawing the tester from the package. The samples in the bucket are melted at the lowest possible temperature, stirred until cold, bottles filled, and sealed as before.

Liquids, Turbid or Showing a Solid Deposit.—These should be gently warmed with frequent shaking, until the deposit is redissolved and the whole has become homogeneous, before the analysis is proceeded with, and the analysis should be completed before the sample has had time to redeposit. A turbidity which does not disappear on warming is usually due to water, in which case it is sufficient if the bottle containing the sample is well shaken each time any of the sample is taken out.

Semi-Solids and Solids.—When the package is not homogeneous, *i.e.* when containing water, dirt, or when it is a mixture, it must be carefully melted on the water bath at the lowest possible temperature, and the contents of the dish stirred until stiff in the case of solids, or cold if semi-solid, after which the analysis can be proceeded with.

Preparation for Analysis.—It is almost impossible to cover every case; the following is only a general guide.

The only samples the analysis of which one may proceed with without any further precaution are clear liquids and homogeneous solids. Turbid liquids, whether the turbidity is due to water or to the deposition of solid matter, seedy semi-solids,—these may be defined as a mixture of solid grains embedded in a softer paste—and non-homogeneous solids must all be brought into a state of complete uniformity before proceeding with the analysis.

SECTION II.

PHYSICAL PROPERTIES.

The physical condition of the sample should always be noted: whether clean or dirty; if fluid, whether clear or turbid; if containing a deposit, what is the nature of the deposit; if semi-solid, whether homogeneous or seedy; if solid, whether homogeneous, dry or greasy, crystalline or amorphous.

Colour is always a point of great commercial importance; it may be taken as a general rule that the paler the colour of an oil or fat the higher is its commercial value, but it is only in very rare cases that the colour is quantitatively measured.

SPECIFIC GRAVITY.

For general purposes the specific gravity bottle with perforated stopper is probably the best, and the 10-gramme bottle a convenient size; the 25-gramme bottle is only required for glycerine, and this because of the high price of glycerine; and because it is always sold as having a certain gravity, the latter requires to be determined with great accuracy. It is better to buy the specific gravity bottles without a counterpoise, because the counterpoise is very rarely correct, and the bottles must always be carefully calibrated before use. When calibrating, the main points to watch are, that no air bubble is left under the stopper, and that the bottle has stood for at least ten minutes at 60° F. before it is taken out of the water for weighing. Duplicate determinations with liquids should agree to within three units in the fourth decimal place; with solids two determinations should only differ in the fourth place of decimals.

The specific gravity of substances insoluble in alcohol may be determined with a fair amount of accuracy by placing a few small pieces of solids or a few drops of liquids in a small beaker, and adding a mixture of alcohol and water, until the sample neither sinks to the bottom nor floats on the surface, but comes to rest between the top and the bottom of the mixture; the mixture is then poured into the gravity bottle, brought to 60° F. and weighed, the gravity found being that of the sample taken. When using this method it is better to mix the alcohol and water first, and allow to stand a few minutes, in order to get rid of air bubbles, before putting the sample in; this saves time, as air bubbles always form on first mixing the alcohol and water.

VISCOSITY.

In this country Redwood's viscometer is the standard instrument; the following factors will allow of easy conversion from one to another:—

Jackson at 70° F. is 3·92 times Redwood at 70° F.
Coleman-Archbutt for 100 c.c. is equal to Redwood at same temperature.
Engler's figures are 25·5 times ,, ,, ,,
,, in seconds are 0·59 times ,, ,, ,,
Hurst's figures are 3·85 times ,, ,, ,,
Saybolt at 70° F. multiplied by 1·71 equals ,, ,, ,,
,, at 212° F. ,, 0·80 equals ,, ,, ,,
Lamansky-Nobel figures are 22·13 times ,, ,, ,,

The lag during the flow of 50 c.c. from Redwood's viscometer is very large, and yet the proposal made by Allen thirty years ago, to deliver the oil under a constant head, apparently found no favour.

TABLE SHOWING LAG IN ACTUAL TEST.

Russian, 895; Temperature, 70° F.

Volume run out.	Seconds.	Lag.
10 c.c.	68	...
20 ,,	142	6 secs.
30 ,,	225	21 ,,
40 ,,	318	46 ,,
50 ,,	420	80 ,,

Agreement between duplicate results with Redwood's Viscometer.

EXAMPLES OF TESTS OF OILS.

RUSSIAN, 907.

Temperature °F.	First Test.	Second Test.	Per cent. Difference.
70	1265	1226	3·1
140	128	128	nil.
180	63	62	1·6
212	46	45	2·2
AMERICAN PALE, 900/905.			
70	470	465	1·1
140	79	78	1·3
180	60	58	3·3
212	40	40	nil.
AMERICAN, 912/915.			
70	673	672	0·16
140	94	94	nil.
180	55	55	1·8
212	44	43	2·3

VISCOSITY OF VARIOUS SUBSTANCES (REDWOOD VISCOMETER).

Oil.	Temperature 70° F.	Temperature 140° F.	Temperature 180° F.	Temperature 212° F.
Animal oil, pale	306–412	85	55	44
,, brown	310	82		
Castor oil, firsts	3861	312–366	126–163	78–112
,, seconds	...	288–352	118–148	72–80
Cocoanut, pressed	230	60	44	38
Colza, Belgian refined	366–422	98		
,, English ,,	346–390	100		
,, Stettin ,,	374–425	93–102	61–66	48–50
Cotton oil, American ,,	270–355	84		
,, Bombay ,,	288			
Hempseed oil, crude	203			
Lard oil, A1	381–403			
,, extra winter strained	353	80		
Linseed oil, Calcutta	208			
,, Canadian	188			
Neatsfoot, English filt.	334–385	79–98	63	51
,, ,, unfilt.	385			
,, North American, cold pressed	395–446	89	58	45
,, ,,	...	88	58	46
,, South American	330	87		
Olive oil, Algerian	336	86		
,, Bari	323			
,, Candia	308–324	84–86	55	50
,, Gallipoli	344			
,, Malaga	312	86		
,, fine Spanish	316			
,, Smyrna	328			
Rape oil, refined, Black Sea	346–360	89–95		
,, ,, East India	365–410	90–103		
,, ,, English	371	95		
,, ,, German	390	...	63	
,, ,, Jamba	389	97		
,, low	340			
Seal oil, water white	233–298			
,, Straw	228–298			
Soya bean, refined	240–255	75–83		
Sperm oil, Arctic deod.	141–187	57–65	42	
,, southern	142–175	53–61	41–43	37
Tea seed oil, refined	334	72		
Tung oil	948	156		
Whale oil, No. 0	240–293	66–75	50	42
,, No. 0, filt.	270	71		
,, No. 1, ,,	243–244	76	53	43–44
,, No. 3, ,,	250			
THICKENED OILS—				
East India rape	8053	793–1439	324–590	186–320
Black Sea ,, (ravison)	...	748–757	313–382	168–250
Whale	...	289–375	...	134

Redwood's figures can be calculated to absolute viscosity in dynes per sq. cm. by the aid of the following formula:—

$$n = kdt.$$

where

n = absolute viscosity,
d = density at the temperature °C. at which the viscosity was taken,
t = the number of seconds for 50 c.c. of the sample,
k = a constant.

k must be determined for the Redwood instrument used, and is found from

$$k = \frac{n}{td}$$

the letters having still the meaning given above, using, of course, as standard liquid one of which the absolute viscosity is known (glycerine, phenol, etc.).

If a sample has been heated for any reason, the oil must be allowed to stand overnight before determining the viscosity, because heating has often a considerable effect on the viscosity.

EXAMPLE OF EFFECT OF HEATING.

Oil.	Before Heating.	After Six Hours.	At Temperature
Blown rape	1041	1120	140° F.
Russian 907	1341	1289	70 ,,
American filt. cyl. . .	178	180	180 ,,

The lowering of the viscosity of the Russian 907 oil reminds one of the lowering of the viscosity of colloids by previous heating.

It must not be forgotten that when two or more oils are mixed together it is not possible to calculate the viscosity of the mixture from the figures of the constituent oils.

Two parts of American 900/907 oil were mixed with one part of Russian 907 oil; the viscosity of the mixture was 488 at 70° F. The calculated figure was 612, giving a difference of 124 seconds; even after correction for specific gravity the calculated result was 541. Attempts made to find the law for the reduction of viscosity with rising temperature, and also the law for mixtures, gave such widely different figures, even when calculated from the figures published by Redwood himself, as to be useless.

SURFACE TENSION.

The surface tensions in dynes per square centimetre of fatty and mineral oil are so close together that they are of no value for analytical purposes. The figures given below were determined by the glass tube and balance, and the results calculated by Proctor Hall's formula (Archbutt, p. 48), where T is the surface tension, w the weight required, C1 the inside circumference of the tube, and C2 the outside circumference of the tube. Surface tension in dynes per square centimetre at 13 C.

SURFACE TENSION BY PROCTOR HALL'S METHOD.

Oil.	Surface Tension.
Scotch 880/885 oil	39·34
Russian 895 oil	42·03
,, 907 oil	43·55
American 865 pale neutral	39·55
,, pale 900/907	39·44
,, ,, 912/915	43·26
Arctic sperm oil	44·03
Stettin colza oil	47·60
Castor oil firsts	54·72

REFRACTIVE INDEX.

The various refractometers specially constructed for the examination of oils and fats are not a very good investment, for they either have an arbitrary scale, or else do not cover the whole range required in commercial work. The Pulfrich type of refractometer is free from these objections; the only one that can be raised against the instrument is that the glass cup for containing the oil sometimes comes off when cleaning it out, but if the old cement be carefully removed the cup may be cemented on again with fish glue in a few minutes and the instrument is ready for use again next morning. When replacing the cup care must be taken that it does not encroach on the polished circle in the centre.

The refractive index is one of the properties of oils that has not been made sufficient use of, especially in the examination of mixtures. The German Customs make the refractive index of that portion of the unsaponifiable from wool fat oleines which is insoluble in acetic anhydride one of the two deciding figures in determining whether the oil shall be admitted as an oleine or whether it shall pay duty as a mineral oil. This refractive index shall not exceed 1·5100.

The specific gravity, refractive index, and iodine value are the only strictly additive properties possessed by the oils and fats, and the speed at which the refractive index can be determined at once gives it great importance when dealing with mixtures. Convenient temperatures to work at are 70° and 140° F.

A useful works check in the manufacture of Turkey Red Oils can be obtained from the refractive index, but it must be understood that this only applies to samples made from the same oil, and with the same percentage of sulphonation. If the refractive indices of three or more samples of known test be plotted, and the curve drawn, the determination of the refractive index of an unknown sample will enable its test to be read off from the curve to within 2 per cent. of the result obtained by analysis, and further, both ammonia and soda samples can be read from the same curve.

In the case of wool grease oleines of the same percentage of saponifiable matter there is a direct relation between the cold test and the refractive index; the higher the cold test the lower the refractive index.

Example.—Wool grease oleine cold test 55° F. refractive index 1·4842
,, ,, 40° F. ,, ,, 1·4900.

The effect of redistilling wool grease oleine is to lower the refractive index, and the addition of resin raises the refractive index.

Example.—Distilled wool grease oleine refractive index 1·4842
Redistilled wool grease oleine ,, ,, 1·4900.

The redistilling in this case had been performed by dissolving resin in the oil.

The difference to the refractive index of an oil or fat (not containing more than 10 per cent. of free fatty acids) made by the 10 per cent. of glycerine usually present is about 0·0112; this is also the average difference between the refractive index of the oil and its fatty acids.

The average temperature variation may be taken as being 0·0001 for each degree Fahrenheit.

TABLE OF REFRACTIVE INDICES AT 70° F., VARIOUS SUBSTANCES.

Animal oil, pale	1·4650 to 1·4686
Arachis oil, refined	1·4705 to 1·4745
Blown cotton oil	1·4803
,, East India rape oil	1·4803 to 1·4855
,, Black Sea rape (ravison)	1·4803 to 1·4855
,, whale oil	1·4774 to 1·4813
Boiled linseed oil	1·4833 to 1·4850
,, ,, substitutes	1·4813 to 1·4986
Cameline oil, refined (dodder)	1·4794
Castor oil, pharmaceutical cold drawn	1·4794
,, firsts	1·4794 to 1·4803
,, seconds	1·4793 to 1·4803
,, Calcutta	1·4794
,, Bombay	1·4784
Castor oil, miscible	1·4784 to 1·4813
Cocoanut oil, pressed	1·4566
Cod-liver oil, Canadian yellow	1·4764
,, ,, coast extra pale	1·4803
,, ,, coast brown	1·4794
,, ,, crude pale	1·4774
,, ,, Newfoundland yellow	1·4784
,, ,, Newfoundland racked brown	1·4784 to 1·4794
,, ,, Newfoundland unracked	1·4784 to 1·4794
,, ,, Scotch crude brown	1·4833
Colza oil, refined Stettin	1·4735 to 1·4754
Cottonseed oil, American refined, filtered	1·4735 to 1·4745
,, ,, Egyptian edible.	1·4725 to 1·4730
Distilled liquid resin	1·4938
Hempseed oil, crude	1·4794
Herring oil, pale	1·4813
Japan fish oil, brown	1·4735 to 1·4764
Lard oil, prime	1·4666 to 1·4725
,, Swift's extra winter strained	1·4676 to 1·4686
,, Swift's No. 1 brown	1·4681
,, Swift's No. 2 brown	1·4686
Linseed oil, Baltic	1·4823
,, Calcutta	1·4813
,, Canadian	1·4770 to 1·4810
Maize oil, refined	1·4715
Neatsfoot oil, English, filtered	1·4695
,, ,, unfiltered	1·4676
,, ,, Swift's North American	1·4686
,, ,, South American	1·4695
Olive oil, Algerian	1·4690 to 1·4695
,, Candia	1·4676 to 1·4705
,, Gallipoli	1·4695
,, Grecian	1·4705
,, Levant	1·4690
,, Malaga	1·4686 to 1·4705
,, Messina	1·4686
,, Pharma.	1·4695
,, fine Spanish	1·4703 to 1·4705

TABLE OF REFRACTIVE INDICES AT 70° F.—*continued.*

Olive oil, Smyrna	1·4690
,, substitutes	1·4695 to 1·4754
Rape oil, Black Sea, refined (ravison)	1·4749 to 1·4774
,, East India, refined	1·4745 to 1·4754
,, English, refined	1·4754
,, Jamba, refined	1·4745
,, Japanese, refined	1·4735
Salmon oil, Californian	1·4814
Sea elephant oil, No. 1	1·4739 to 1·4762
Seal oil, water white	1·4754 to 1·4774
,, straw	1·4745 to 1·4785
Shark liver oil, refined	1·4725
Soya bean oil, crude	1·4754
,, ,, refined	1·4754 to 1·4774
Sperm oil, Arctic No. 1	1·4674 to 1·4686
,, ,, ,, 2	1·4600 to 1·4676
,, Southern	1·4656 to 1·4760
Tea seed oil, refined	1·4705 to 1·4715
Whale oil, No. 0, filtered	1·4748 to 1·4764
,, ,, 1, unfiltered	1·4725 to 1·4735
,, ,, 1, filtered	1·4735 to 1·4740
,, ,, 2, unfiltered	1·4715
,, ,, 2, filtered	1·4752
,, ,, 3, unfiltered	1·4705 to 1·4715
,, ,, 3, filtered	1·4739
,, Japanese yellow	1·4715
Fatty acids from 47 per cent. wool grease oleine	1·4735
COMMERCIAL FATTY ACIDS—	
Arachis oil fatty acids	1·4666
Castor oil fatty acids, firsts	1·4705
,, ,, seconds	1·4705
Linseed oil fatty acids	1·4686
Maize oil fatty acids	1·4650
Rape oil fatty acids	1·4715
Soya bean oil fatty acids	1·4670
95 PER CENT. OLEINES—	
American white	1·4632 to 1·4676
,, brown	1·4621 to 1·4696
Australian white	1·4626 to 1·4676
,, brown	1·4614 to 1·4676
Belgian white	1·4626
,, brown	1·4626 to 1·4687
Cotton oleine, filtered	1·4705 to 1·4715
Dutch white	1·4616 to 1·4621
,, brown	1·4636
English white	1·4646
,, brown	1·4645 to 1·4700
French white	1·4646 to 1·4650
,, brown	1·4636 to 1·4666
OLEINES FROM RECOVERED PRODUCTS—	
English pure 45 % sap.	1·4833
,, ,, 47 ,,	1·4822
,, ,, 49 ,,	1·4803
,, ,, 50 ,,	1·4813

OLEINES FROM RECOVERED PRODUCTS—	
English pure 51 % sap.	1·4793 to 1·4818
,, ,, 53 ,,	1·4784
,, ,, 54 ,,	1·4790
,, ,, 55 ,,	1·4725
,, ,, 56 ,,	1·4789
,, ,, 58 ,,	1·4774
,, ,, 60 ,,	1·4754
,, ,, 65 ,,	1·4705 to 1·4735
,, ,, 70 ,,	1·4708 to 1·4738
French pure 50 ,,	1·4735 to 1·4881
Cotton oleine, 50 ,, filt.	1·4852
,, ,, 70 ,, ,,	1·4735
SULPHONATED OILS—	
70 % castor	1·4416 to 1·4486
60 ,, ,,	1·4405
50 ,, ,,	1·4256 to 1·4266
40 ,, ,,	1·4007
Pale soluble leather oils	1·4276 to 1·4491
Dark ,, ,,	1·4695
70% from 70% recovered oleine	1·4656
Monopol oil	1·4371
Turpentine, American	1·4705
,, substitute	1·4376
UNSAPONIFIABLE MATTER FROM—	
Black oil, 60% sap.	1·4995
70% recovered distillate	1·5033
50 ,, ,,	1·5051
Recovered stearine 102 M.P.	1·5134
50% recovered oleine	1·4929
MINERAL OILS—	
American half white oils—	
8486 spec. grav.	1·4715
8576 ,,	1·4754
8582 ,,	1·4739
8590 ,,	1·4750 to 1·4759
Russian half white oils—	
835/40 spec. grav.	1·4661
845/50 ,,	1·4710 to 1·4732
855/60 ,,	1·4756
860/65 ,,	1·4750 to 1·4861
880/85 ,,	1·4823
890/95 ,,	1·4794
American mineral oils—	
Mineral colza.	1·4576 to 1·4586
840 sun-bleached neutral	1·4646
850 neutral spindle	1·4752
865 ,,	1·4752
875 pale	1·4919
885 ,,	1·4938 to 1·5051
885/90 neutral	1·5001
900/5 pale	1·5033 to 1·5235
900/7 ,,	1·5051 to 1·5088
912/15 ,,	1·5088 to 1·5154
910/15 red	1·5107 to 1·5152
920/5 ,, Kansas	1·5170
900 pale Mexican	1·4995

TABLE OF REFRACTIVE INDICES AT 70° F.—*continued.*

915 pale Mexican	1·5075
920/5 pale Texas	1·5130 to 1·5143
930/5 ,,	1·5183 to 1·5192
Galician 885 pale	1·4910 to 1·4980
,, 900/5 ,,	1·5051
,, 915/17 ,,	1·5088
Russian 895 pale	1·4929 to 1·4964
,, 900 pale	1·4986
Russian 907 pale	1·4986 to 1·5061
Scotch 840/60 cleaning oil	1·4764
,, 860/8	1·4852 to 1·4933
,, 885/90	1·5023 to 1·5061
Resin oil, pale neutral	1·5386
,, ,, refined	1·5133 to 1·5538
,, refined	1·5428
,, grease making	1·5386

ROTATORY POWER.

Mineral Oils.—The rotation of mineral oils has acquired some importance of late years, as it must have a direct bearing upon the question of origin, but the amount of this rotation is so small that it has no value for analytical work.

Wool Grease Oleines.—All are dextro-rotatory, and have a very pronounced rotation, but it is not as high as that of the grease from which they are made.

Example.—Hard Yorkshire grease,	specific rotation 13·7
Oleine from the same grease,	,, ,, 11·6.

The rotation of recovered grease oleines as a class varies from 6·9 to 14·7. The rotation of the unsaponifiable matter from wool grease oleines is again higher than that of the oleine itself, varying from 12 to 29·4.

The German customs authorities have made the rotation of that portion of the unsaponifiable matter which is insoluble in acetic anhydride one of the standard figures in deciding whether a recovered grease oleine is pure or whether it shall be taxed as mineral oil. In order to pass as oleine the rotation of the unsaponifiable matter insoluble in acetic anhydride must not be lower than 18, and yet, as shown above, the rotation of the whole unsaponifiable matter from pure samples often falls below the limit. The latter, therefore, appears to have been fixed on insufficient data.

MELTING POINT.

The standard method is the capillary tube, and this method should always be used in all disputes.

A fairly accurate, and very rapid, method for works purposes is carried out by placing a thermometer in a test tube, and pouring into the test tube sufficient of the melted sample to cover the thermometer bulb, warming if necessary until the sample is completely fluid, and the whole is quite clear; then stir constantly until the first sign of turbidity is seen. This point is the melting point of the sample.

Example.—A stearine gave 130° F. by this method; the same stearine

in closed capillary (newly filled)	melts at 128° F., clear at 134° F.
in ,, ,, (stood 24 hours)	,, 129° F. ,, 131° F.
in open ,, (newly filled)	the sample rises at 130° F.
Bensemann	melts at 129° F., clear at 133° F.
Pehl	clear at 130° F., rises at 133° F.

Open Capillary Method.—Fill the sample into an ordinary capillary, and when the sample has set again break off the closed end of the tube; fix to a thermometer and heat as usual; record as the melting point the temperature at which the sample in the tube commences to rise towards the top of the liquid in the beaker.

This method gives results in fairly close agreement with the closed capillary, and has the advantage of being available for all samples, whether light or dark coloured. This cannot be said for the closed capillary, which is useless for all dark-coloured samples, or for transparent bodies like resins. In the case of resins the rise of the column of melted resin up the tube is very slow; in extreme cases the rise may be prolonged over many degrees. This is caused by the very high viscosity of some resins at temperatures near the melting point, hence the need for reading the thermometer as soon as the column starts to rise up the capillary.

RESINS.	MELTING POINT IN OPEN CAPILLARY.
French (K)	207° F.
,, (WW)	209 ,,
,, (extra)	207 ,,
American (H)	204 ,,
,, (K)	205 ,,
Greek (colour like American H)	208 ,,

PITCHES.	MELTING POINT IN OPEN CAPILLARY.
Wool grease pitch	125° to 157° F.
Wool grease stearine pitch	157 ,,
Pitch from 70 per cent. black oil	151 ,,

The above figures give some idea of the variation of these pitches; the melting point of fatty pitches gives no indication as to the origin of a sample. The reason is that the manufacturer is able to produce any melting point he wishes, and also that the extent to which the distillation is carried may vary for many reasons, such as change in values, etc.

The only class of sample for which the open capillary is useless is the pitch resulting from the distillation of some classes of fatty acids, which when heated to melting forms a frothy mass, neither fluid nor solid, and cannot be induced to run to the bottom of the capillary.

KRAMER and SARNOW's method for taking the melting point of dark-coloured samples is used on the Continent, and is carried out as follows:—

An open tube, inner diameter 5·7 mm., is dipped into the molten sample for a depth of 5 mm., the forefinger being placed over the other end of the tube and kept there until the sample has solidified. The outside of the tube is cleaned, and exactly 5 grammes of mercury poured on to the top of the column of sample in the tube. The tube is clamped to a thermometer, which is then immersed in a beaker of saturated brine, and the beaker heated. The temperature at which the globule of mercury falls through the sample is noted as the melting point of the sample.

The results obtained in this way bear no relation whatever to those obtained by other methods, and may be as much as 40° F. lower, but duplicates are very concordant. It has lately been found that differences arise between different observers, and the proposal has been made that the tube shall be exactly 6 mm. internal diameter, and be dipped 7 mm. into the molten sample instead of 5 mm., in order to have a depth of sample of 5 mm. after cooling; but it does not appear that even this will stop discrepancies in the case of frothy samples like the fatty acid pitches mentioned above, because the amount of actual sample retained in the tube is certain to vary according to the extent to which the sample in hand is liable to froth.

TITRE TEST.

This test is of value chiefly to the soap and candle maker, and the higher the titre test of the sample the greater its value.

The test is quite useless for all samples having a titre lower than 80° F., because such samples give almost any figure the operator wishes, provided one knows when to stir the sample during solidification.

In this country all tallows are sold on Norman Tate's results, which are obtained as follows.

The following method for the examination of fats (tallow) for setting point (titre) has been devised by A. N. Tate of London:—

Procedure.—(*a*) Thoroughly mix and average the sample.

(*b*) Take a weighed amount, say 50 grammes of the sample, and melt it completely in a basin over a boiling water bath.

(*c*) Add to the melted tallow, whilst still warm, a mixture of 40 c.c. of a solution of caustic soda of 36 Be. (sp. gr. 1·36) and 25 c.c. of absolute alcohol (methylated spirit may be used).

(*d*) Stir continually until the resultant soap solidifies.

(*e*) Next pour gradually on to the soap while stirring about 1·5 litres of hot water (distilled), and boil until the solution is reduced to 0·75 litre.

(*f*) Add to the solution 25 c.c. of sulphuric acid previously diluted with 500 c.c. of distilled water to thoroughly decompose the soap.

(*g*) Allow the fatty acids in a melted condition to separate and float on the top; when cold, syphon off the water.

(*h*) Carefully remove the cake, and melt as described at "*a*." Care must be taken, before proceeding to test the setting point, to note that the saponification has been complete, and if the fat is not quite free from water it may be melted in a small separator funnel and the water drawn off, and the fat itself run off into the testing apparatus.

The Apparatus.—(*a*) A clear class cylindrical vessel having an inside measurement of 9 cm. high and 2·75 cm. diameter, and sides 0·3 cm. thick, slightly rounded at the bottom, and provided at the top with a glass lip or ebonite flange on which to hang it.

(*b*) An outer vessel of clear glass 13 cm. deep and 10 cm. wide for the protection of the inner cylinder from draughts.

(*c*) An ebonite or wooden cover (not metal) with a hole in the centre and slightly depressed flange, on which to hang the flange of the inner cylinder.

(*d*) Two small pins to keep the cylinder in position during stirring.

(*e*) An accurate thermometer[1] graduated from about 5° to 70° C. in tenths of a degree; the size of the bulb to be as nearly as possible 2·5 cm. in length, and 0·60 cm. in diameter.

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[1] Tate recommends M. Baudin, 276 Rue Saint Jacques, Paris, who makes a thermometer admirably adapted for this purpose.

(*f*) An upright pillar, provided with

(*g*) An arm, from which to suspend the thermometer, and fastened into

(*h*) A stout stand or base of wood, hollowed slightly to receive the larger glass vessel and keep it in its exact position.

The Process.—A. Melt the fatty matter in a water bath, carefully avoiding temperatures higher than 70° C., and pour into the smaller cylindrical vessel, until the fat in it stands to the height of about 6·5 cm.

B. Should the fat not be perfectly liquid, the inner vessel may be put in the bath to remelt the mass. Do not hold it over a Bunsen flame, and watch that the temperature does not rise above 70° C.

C. Place the cylinder with the fat in, in the outer vessel, and so fix the thermometer that it shall hang (the bulb) in the centre of the fat. Next stir continually, by giving the thermometer a quick circular movement, without allowing it to touch the sides of the vessel, but taking care that all solidifying particles as they form are well stirred into the mass.

The mass will gradually become clouded throughout and the mercury descend until it remains some moments stationary. Then stir gently three times to the left, and three times to the right, taking care that the bulb of the thermometer does not touch the sides of the vessel.

The mercury will commence to remount; note the point to which it ascends, and take this point as the setting point of the fat.

Freedom of the Fat from Water.—It is essential that the fat before being placed in the testing apparatus shall be free from water, but during the removal of the water it is necessary that no higher temperature than 70° C. be used, and that prolonged subjection to this temperature should be avoided. Some operators take the cold cake of fat and press it between the folds of blotting paper. This is objectionable, as oftentimes a portion of the softer fat is absorbed by the paper. Also be sure that the fat is saponified thoroughly.

SOLIDIFYING POINT.

This is, especially in the mineral oil trade, taken at the point at which the sample first shows a dullness on the surface when cooled in a beaker.

COLD TEST.

The methods for taking the cold tests of oils are very varied, and unless the sample is carefully freed from impurities and moisture, and a very great deal more time spent over it than the value of the results warrant, the results are as varied as the methods of obtaining them.

The cold test of lubricating oils varies with the care used in the removal of solid paraffins at the works, and of oleines and seed oils with the temperature of the press room, the temperature of the material pressed, and the amount of pressure used, so it is obviously useless to give figures.

It is essential that the cold test be taken of lubricating oils for outside purposes, and of oils for refrigerating machines, the cold test necessary varying with the temperature to which the oil may be exposed.

The test finds its greatest use in works practice, where it is often necessary to turn out large quantities of material with no more than a given variation in cold test, and as from some materials it is impossible to keep within the prescribed limits, this test is useful in checking the mixing necessary to obtain the required figures.

Method.—Place a thermometer in a ½-inch test tube; then pour into the tube sufficient of the sample to cover the bulb of the thermometer. An 11-cm. filter paper is now pinned round the test tube, carbon disulphide dropped on to the filter paper until the paper is soaked, and the oil constantly stirred with the thermometer; more carbon disulphide is dropped on to the paper as required, and the stirring continued until, on inverting the test tube, the oil no longer runs down the side of the tube. This point is read off and reported as the cold test of the sample.

VAPOURISING POINT, FLASH POINT, AND FIRE POINT.

Closed Test.—For oils of low flash, like lamp oils, etc., Abel's tester is used; for lubricating oils and cylinder oils the Pensky-Martin or Gray's tester are used.

Open Test.—Heating in a beaker or dish is the usual practice. On commencing to heat the beaker or dish, the surface of the oil is carefully watched, and the first sign of vapour on the surface of the oil is noted and the temperature read off as the vapourising point of the oil. From this point the heating is continued, and a flame of pea size, best obtained by using a mouth blowpipe as jet, is passed across the dish or beaker at a distance of half an inch above the surface of the oil. The temperature at which a blue flame runs all round the pot is recorded as the open flash point of the sample. On still continuing the heating, and frequently applying the blowpipe jet to the surface of the oil, the temperature at which the oil continues to burn after taking away the flame is noted as the fire test. Immediately this occurs the thermometer must be taken out of the oil or it may be spoiled.

TABLE OF OPEN FLASH POINTS.

	Degrees Fahrenheit.
Castor oil, firsts	562
,, seconds	534
Cocoanut oil	394
Cotton oil, refined	567 to 600
,, greases, black	360 to 366
,, stearines	354
Colza oil, refined	516 to 600
Cod oil, Malabar	412
Japan fish oil	436 to 538
Lard oil	529 to 600
Linseed oil	over 600
,, boiled	422
Neatsfoot oil	496 to 592
Neutral wool fat	498 to 500
Olive oil	390 to 450
,, sulphur	194 to 400
Palm oil, bleached	341
Rape oil, blown	516
Sperm oil	458 to 502
Salmon oil	450
Tallow oil	419
Candle-maker's oleines	330 to 370
Oleines from recovered products	330 to 360

DISTILLATES—		Degrees Fahrenheit.
Sap.	Source.	
55 per cent.	Hard grease	330 to 352
80 ,,	Soft ,,	346
65 ,,	Hard ,,	334
90 ,,	Black oil	332 to 340
85 ,,	Soft grease	344 to 351
99 ,,	,,	343
75 ,,	Black oil	359
50 ,,	Redistilled recovered oleine	339
95 ,,	Soft grease	346
STEARINES—		
M.P.	Source.	
115° F.	Hard grease	359
90° F.	Soft ,,	346
106° F.	Hard ,,	352
112° F.	Black oil	341 to 354
100° F.	Soft grease	348
110° F.	,,	342 to 348
94° F.	,,	341 to 343
90° F.	,,	340
132° F.	Hard grease	386
103° F.	Black oil	358
98° F.	Hard grease	328 to 336
104° F.	Black oil	329

VOLATILITY AT 212° F.

In commercial work the question often rises as to what is the maximum loss that a sample would show on heating.

This volatility is most variable, and may, in the case of the spirit oil obtained at the beginning of recovered grease distillation, rise to over 90 per cent.

The sample should always be filtered through a dry filter paper if there is any suspicion of water being present.

Not more than 1 gramme of the sample is weighed accurately into a Petri dish of 2½ inches diameter, and the dish heated in the boiling-water oven until the difference between two weighings does not exceed 2 milligrammes.

Sample.	Loss at 212° F.	Sample.	Loss at 212° F.
	Per cent.		Per cent.
American dark cylinder oil	0·05 to 7·16	Pressed black oil	2·66
,, brown oleine, 95 per cent.	0·67	Dry cleaner's oleine residue	9·93 to 55·60
Belgian brown oleine, 95 per cent.	0·43	Recovered oleines, 80% sap.	0·94
Boiled oil substitute used for core oil	19·56	,, ,, 70 ,,	0·99 to 1·51
,, ,, ,,	19·13	,, ,, 60 ,,	0·61
,, ,, ,,	27·25	,, ,, 50 ,,	0·82
,, ,, paint oil	24·75 to 36·47	Scotch mineral oil, 865 sp. gr.	21·53
Extracted black oil	10·24 to 29·35	,, ,, 885 ,,	2·28
		Transformer oil, Galician	3·27
		Spirit oil from grease distillation	91·76

SECTION III.

CHEMICAL EXAMINATION.

WATER.

Detection.—Water can always be detected by heating a few grammes of the sample in a porcelain dish over a ring Argand burner which has been turned down until the flame is non-luminous; if water be present it will rise in the form of bubbles through the hot sample.

The Argand is the most useful form of burner in an oil works laboratory; when turned down until the flame becomes non-luminous, fats may be left over the burner for quite a while without any fear of burning.

Estimation.—In mixtures containing light mineral oils, oils with iodine values, sulphonated oils from oils of high iodine values, lubricating greases, emulsion oils, etc., accurate results can only be obtained by distillation.

Twenty-five grammes of the sample are mixed with 50 c.c. of xylene and distilled. The distillate is collected in a graduated cylinder, and the distillation continued until no more water comes over with the xylene. The water collects below the xylene in the cylinder. If any drops of water adhere to the sides of the cylinder they may be coaxed down to the rest of the water with a glass rod. When quite cold the number of c.c. of water are read off, the result multiplied by 4 giving the percentage of water in the sample.

For ordinary samples about 2 grammes of the sample are weighed into a small beaker containing a glass rod, and the beaker heated in the water oven until the sample is quite clear and free from small water drops on stirring with the glass rod. The beaker is then cooled and weighed. It is quite useless to heat and weigh in an attempt to arrive at constant weight; if this be done the results in many cases will not be as accurate as by the above procedure owing to lactone formation, oxidation, etc.

For works purposes it will be found much quicker to take a porcelain dish (size 00), put in a small glass rod, weigh into the dish about 10 grammes of the sample and heat over a non-luminous Argand flame, the dish being stirred continually until no more bubbles are given off: the heat must not be sufficient to cause the sample to give off fumes. The dish is then cooled and weighed. The loss of weight gives the amount of water in the sample.

ASH IN OILS AND FATS.

Weigh into a platinum dish 5 grammes of the sample; heat slowly until the sample is charred, and incinerate at the lowest possible temperature; cool in a desiccator, and weigh. If an analysis of the ash is required, it is better to repeat the process several times in the same dish, rather than ashing a larger quantity at first.

A complete analysis of the ash can then be made or any special constituent sought for.

EXAMPLES OF ASH IN OILS AND FATS.

	Per cent.		Per cent.
85 per cent. Black oil	0·63	Hempseed oil, crude	0·04 to 0·06
80 ,, ,,	1·07	Neutral wool fats	traces to 0·19
70 ,, ,,	2·68	Linseed oil, Canadian	0·14
60 ,, ,,	0·38	,, Plate	0·05 to 0·20
Bone fats	traces to 1·29	Olive and Oleine grease	0·16
Cotton oil, Egyptian, refined	0·01 to 0·08	Recovered stearines	0·01 to 0·03
Grease, pale hard, Yorkshire	0·37	Whale oil fatty acids, commercial	0·05 to 0·07
,, medium ,,	0·26		

NON-FATTY MATTER.

The only class of samples in which visible dirt can usually be *seen* are footy samples of fatty oils, but non-fatty matter in a very finely divided state may be present to the extent of 30 to 40 per cent. Fatty bodies of all descriptions really should be water free before starting to determine the non-fatty matter, and for this reason it is much better to take the residue from the water estimation, dissolve this in methylated ether (about 50 c.c.), and filter through a dried and tared filter paper. The filter paper is then washed with ether until fat free; and it is easy to tell when this is the case, because when fat free the filter paper no longer shows transparent spots or margin.

In the case of recovered products, extracting in a Soxhlet offers very little advantage unless the sample gives a clear ether solution, because the ether runs back into the flask quite turbid, and has to be filtered afterwards. This filtration is often very slow owing to the finely divided non-fatty matter stopping up the pores of the filter.

In the case of bone fats and commercial fatty acids the above process is liable to error unless the sample is free from metallic soaps; for example, a sample of commercial fatty acids gave 9·21 per cent. of non-fats on extraction with ether, but on boiling 10 grammes of the sample with dilute hydrochloric acid until the fatty layer was quite clear, cooling and pouring into a separator, the aqueous layer being run off, the fat dissolved in ether, and washed with water until acid free, and the ether run through a dried and weighed filter, the amount of non-fatty matter was 0·16 per cent. Foots from fatty oils may also contain oxidised fatty acids insoluble in ether, and unless the ether residue be extracted with hot absolute alcohol before weighing, the non-fatty matter may be up to 15 per cent. in error.

FREE FATTY ACIDS.

Volumetric Estimation.—The volumetric method is usually used for commercial work, and the results always calculated on the mean molecular weight of 282, which is that of oleic acid.

The accuracy of the titration varies with the variation of the molecular weight of the fatty acids present in the sample, and as these vary from 260 to over 400, the result of a titration on 282 may be almost 50 per cent. in error. The titration does not take many minutes, and when the molecular weights are approximately known, it is very convenient.

Two grammes of the sample are dissolved in 50 c.c. of alcohol (previously neutralised with N/10 alkali, using phenolphthalein as indicator) and 25 c.c. of motor spirit. Titrate the solution with N/10 potash, shaking all the time (if not well shaken the colour change is rather slow). The deduction to be made for the petrol is 0·1 c.c. The number of c.c. of N/10 potash required when multiplied by 0·14 gives the percentage of free fatty acids calculated to oleic acid.

The conversion of acid values to oleic acid may be done with sufficient accuracy by dividing the acid value by 2 (actual divisor 1·98).

For commercial fatty acids, recovered greases and their products, candlemaker's oleines, stearines, etc., weigh and dissolve as before, but titrate with N/4 potash, and no deduction need be made in these cases.

The following table will be found useful if copied out and hung by the side of the N/4 potash burette when many such titrations have to be made :—

c.c.	Per cent. Oleic.	c.c.	Per cent. Oleic.	c.c.	Per cent. Oleic.
1	3·53	8	28·20	15	52·88
2	7·05	9	31·73	16	56·40
3	10·58	10	35·25	17	59·93
4	14·10	11	38·78	18	63·45
5	17·53	12	42·30	19	66·98
6	21·15	13	45·83	20	70·50
7	24·68	14	49·35	21	74·03
0·1	0·35	0·4	1·41	0·7	2·47
0·2	0·71	0·5	1·76	0·8	2·82
0·3	1·06	0·6	2·12	0·9	3·17

Gravimetric Estimation.—Weigh 2 to 10 grammes of the sample, according to the amount of free fatty acids shown by the titration, into a 300 c.c. flask ; dissolve in 30 c.c. of petrol-ether (sp. gr. 0·64), warming if necessary ; when cold add 25 c.c. of alcohohic potash (roughly N/1), shake well, and pour into a separator. After separation has taken place, run the soap solution off, wash the petrol in the separator twice with cold water (25 c.c. each time), and once with 25 c.c. of spirit which has been previously saturated with petrol ; after washing, run the petrol into a weighed flask, repeat the extraction and washing twice more, running the petrol from each extraction into the same flask, then distil the petrol off, and heat the flask in the water oven until the residue in the flask is free from petrol. Cool, and weigh. The residue in the flask consists of neutral fats and unsaponifiable. The weight of sample taken, minus the residue in the flask, equals the free fatty acids in the sample.

If further examination of the free fatty acids is required, the soap solution and washings are united, heated on the water bath until all the alcohol is driven off, the soap taken up in water, decomposed with acid, and the fatty acids shaken out with ether meth. in a separator, the acid liquor run off, and the ether washed with water until acid free—four washings are usually sufficient. The ether is then run into a weighed flask, the ether distilled off, the contents of the flask dried in the water oven, cooled, and weighed.

SEPARATION OF NEUTRAL FAT AND UNSAPONIFIABLE.

The petrol residue from the free fatty acid estimation is saponified by boiling for thirty minutes under a reflux tube with alcoholic potash about N/1, using 25 c.c. for every 2 grammes taken. Next add 10 c.c. of water for every 25 c.c. of alcoholic potash used, then shake out three times with petrol-ether, sp. gr. 0·64, using 30 c.c. each time and washing each lot of petrol twice with water and once with alcohol which has been previously saturated with petrol, keeping both the soap solution and the washings. Run the three petrol extracts into the same weighed flask. The petrol is next distilled off, the unsaponifiable dried in the oven, cooled, and weighed. The unsaponifiable should be kept for further examination. With the exceptions of Sperm oil, Shark liver oil, and Crude whale oil the above process may be used universally; crude whale oil is included amongst the exceptions because it sometimes contains crude sperm oil.

Unsaponifiable in Sperm Oil, Shark Liver Oil, and Crude Whale Oil.— Saponify 2 grammes as before, and then drive off the alcohol on the water bath until the soap in the flask only smells faintly of alcohol; dilute with 50 c.c. of water, and extract three times with ether meth., washing each lot of ether twice with water, keeping the soap solution and washings as before. If the above be carefully done, no trouble will be caused by emulsions, which form both in absence of alcohol and also when too much alcohol is present.

We have no means of separating the neutral fat in a sample as such, but can only separate the fatty acids from it,—that is, the combined fatty acids of the sample—and examine them.

The soap solution and washings from the unsaponifiable estimation are united, evaporated down on the water bath until alcohol free, the soap taken up in water, decomposed with acid, and poured into a separator and shaken out with ether twice, each time washing the ether with water until acid free; the ether is then distilled off, and the fatty acids in the flask dried in the oven, cooled, and weighed. The fatty acids are kept for further examination. The total saponifiable contents of the sample consist of the free fatty acids plus the combined fatty acids.

IODINE VALUE.

The iodine value of oils and fats is of the greatest value when the purity of a single oil or fat is in question, or when determining the composition of a mixture, if the constituents but not the proportions are known. The additive nature of the iodine value makes it possible to calculate what the iodine value of a mixture of any number of oils will be, provided always that we know the iodine values of the oils used in making the mixture. This additive nature of the iodine value also means that the presence of semi-drying or drying oils in a mixture can be completely covered up by mixing with oils of low iodine value. This of course very much reduces the usefulness of the iodine value when examining mixtures, and after all in commercial work far more mixtures are met with than pure oils. Mixed oils can be found on the market with an iodine value of from 60 to 70 and yet containing a heavy percentage of semi-drying oils.

When it comes to the matching of a mixture, additive figures are necessary, and the only additive figures we have are specific gravity, refractive index, iodine value, and saponification value.

Many processes have been brought forward for the determination of the iodine value, but the original method of Hubl is still the standard; and if care be taken to have an excess of 100 per cent. of iodine still present when the absorption is at an end, the only objection that can be raised to the process is the time required, and even this objection can be largely done away with if the oil be weighed out and the iodine added last thing in the afternoon, allowing to stand overnight, and the titration be performed next morning.

The Hubl Process.—25 grammes of resublimed iodine are dissolved in 500 c.c. of absolute alcohol, and 30 grammes of mercuric chloride are also dissolved in another 500 c.c. of absolute alcohol. These solutions are kept separate and the amount required prepared by mixing equal quantities of the two solutions twenty-four hours before using. For the titration, 24 grammes of sodium thiosulphate are dissolved in 1 litre of distilled water.

Volhard's method of standardising the sodium thiosulphate is very convenient, and the only solution required is made by dissolving 3·8774 grammes of pure fused potassium dichromate in 1 litre of distilled water. This solution will keep indefinitely. 10 c.c. of a 10 per cent. solution of potassium iodide, 5 c.c. of hydrochloric acid, and 20 c.c. of the dichromate solution are mixed in a porcelain dish, diluted with 50 c.c. of water, and titrated with the thiosulphate solution until the solution is straw coloured. 1 c.c. of a 0·5 per cent. solution of starch is added as indicator, and the titration continued until the blue colour of the solution just disappears. The thiosulphate solution should be dropped into the dichromate, not run in, as when added too quickly it is more difficult to obtain results which agree. Two titrations should not differ by more than 0·1 c.c. of thiosulphate. Since each cubic centimetre of the dichromate solution liberates 0·01 gramme of iodine, the 20 c.c. used will liberate 0·2 gramme of iodine.

The chloroform used as solvent for the sample should be the purest that can be obtained, preferably Duncan's B.P. Carbon tetrachloride may be used as solvent in place of the chloroform.

Amount of oils and fats to be weighed out:—

0·1	gramme	of	resins.
0·15	,,	,,	drying and semi-drying oils.
0·3	,,	,,	non-drying oils.
0·5	,,	,,	solid fats.
1·0	,,	,,	mineral oils, mineral waxes, and white stearines.

The sample is weighed in a weighing bottle, and the requisite number of drops dropped into a 12-oz. narrow-mouthed stoppered bottle, dissolved in 10 c.c. of chloroform, and 25 c.c. of the mixed iodine and mercuric chloride solution added; the bottle is then stoppered up and placed overnight in a dark cupboard. Next morning 15 c.c. of a 10 per cent. solution of potassium iodine are run round the bottle stopper and neck, 150 c.c. of distilled water added, and the bottle shaken; the excess of iodine is then titrated back with the thiosulphate solution, using starch solution as indicator. During the titration, if the bottle be rotated in an upright position on the bench, and then tipped to an angle of 45 degrees whilst the contents are still rotating, this method of shaking will be found to aid the extraction of the free iodine from the chloroform and shorten the time required for the titration. One blank test should be put on for every ten tests that are started together; this blank should be titrated after the fifth test. If the number of tests is more than ten, one blank must be titrated before the first test and the second blank after the last test, and the average of the two taken as the titration of the blank.

If Wijs' method is used it is much cheaper to prepare the iodine chloride in the laboratory by dissolving 13 grammes of iodine in 1 litre of glacial acetic acid, and pass a current of chlorine through the solution until the colour of the solution changes to a decidedly paler shade. The solution thus obtained is used in the same way as the Hubl solution, except that the time is so much shortened that in every case the titration can be made after only four hours' standing. This will be found long enough even for resins which have the highest iodine value of any oil or fat yet examined. A further advantage is, that the solution is so stable that a blank need only be made every month.

TABLE OF IODINE VALUES.

Animal oil, pale	54·2 to 71·6
,, brown	63·3
Arachis oil, refined	83
Black oils	40·1 to 81·9
,, extracted	19·3 to 36·0
,, pressed	19·1
Blown cotton oil	55·9
,, East India rape oil	52·2 to 66·9
,, Black Sea rape oil	66·0
,, whale oil	54·8 to 67·2
Boiled linseed oil	122·1 to 165·3
,, ,, substitute	57 to 109·7
Bone fat, boiled	52·9 to 53·4
,, extracted	54·6 to 58·3
Cameline oil, refined	155·5
Castor oil, firsts	81·7 to 86·7
,, seconds	84·7 to 86·5
,, miscible	79·4
Cod oil, crude dark	165·6
,, ,, British	147·2 to 159
,, ,, Scotch	134·8
,, Coast	134·8
,, ,, Hull	157·4
,, Japanese yellow	147·2
,, Newfoundland yellow	143 5
,, ,, brown	138·4 to 142·8
Cocoanut oil	10·4
,, pressed	8·6
Colza oil, English	94·3 to 113·8
,, German	107·7
,, ,, Stettin	99·5 to 106
Cotton oil, edible Egyptian	105·4
,, Bombay, refined	104
,, refined	99·1 to 103
,, ,, filtered	102 to 107·4
Distillate from Malabar cod fatty acids	57·0
,, Sea elephant oil, fatty acids	65·3
,, Whale oil, fatty acids	74·8
,, 60 per cent. Black oil	54·7
,, Extracted Black oil	16·8
,, Soft greases	52·9 to 64·7
,, Medium grease	36·9 to 51·6
,, Hard grease	40·3 to 49·4
,, Redist. yellow stearine	45·4
,, Gas oil from grease distillation	50·7
Distillate from Seconds of grease distillation	48·2
,, Redistillation of medium grease	36·9
,, Redistilled hard grease (French)	38·0 to 38·1
Fatty acids from—	
Pale animal oil, commer. f.a.	63·6
Castor oil, firsts, ,,	89·1
,, seconds, ,,	89·1
Cotton oil, ,,	106·4 to 111·3
Fish oil, ,,	143·7
Japan fish oil, ,,	123·6
Linseed oil, ,,	167·7
Maize oil, ,,	119·7 to 127·1
Rape oil, ,,	148·9
Soya bean oil, ,,	124·1 to 141
Whale oil, ,,	107·2 to 135·5
Turkey red oil 50%	71·0
60% Black oil	60·1
65% Grease distillate	26·7
70/75% ,,	36·9
Soft grease	57·6
Hard ,,	27·0
50% Oleine	46·7 to 51·2
47% ,,	47·2
Black oil stearine, 100/105 M.P.	26·2 to 29·4
Fish cake, white	72·2
,, yellow	101·6
,, brown	58·8
Gas oil from grease distillation	48·9 to 60·2
Soft greases	25·2 to 84·7
Medium ,,	26·8 to 41·3
Hard ,,	23·8 to 43·8
American half-white oil—	
sp. gr. ·8486	9·1
,, ·8574	9·0
,, ·8590	7·3
Hempseed oil, crude	161·8
Herring oil, dark	110·3 to 117·1
Horse oil	75·7
Hot neck grease	25·7
Hot press oil (candle-maker's)	71·2
Illipe butter	50·3
Japan fish oil	101·9 to 121·1
Lard oil, prime	70·6 to 74·3
,, extra winter strained	69·3 to 75·6
Linseed oil, Canadian	185
,, Plate	171·8

TABLE OF IODINE VALUES—*continued.*

Menhaden oil, straw	147·2
,, brown	165·2 to 189·6
American pale mineral oils—	
Mineral colza, Penna	2·4 to 8·0
860/865 neutral, ,,	8·8 to 11·2
880/885 ,,	10·4
880/885 ,,	15·5 to 18·4
885/890 neutral, ,,	12·4
890/895 ,,	6·7
900/905 ,,	11·7
900/907 ,,	9·7 to 10·5
905 ,,	8·4 to 11·1
912/915 ,,	7·9 to 8·5
900 spindle, Mexican	7·6
920/925 pale Texas	9·2
930/935 ,,	9·2
American red mineral oils—	
912/915 Penna	10·7 to 15·3
925/930 Kansas	8·9
920/930 Texas	12·4 to 22·1
930/940 ,,	12·9
American filtered cylinder oils—	
885/890 high cold test	6·9 to 10·3
880/890 low cold test	8·8 to 13·3
Dark cylinder oils	11·3 to 17·7
American black mineral oils—	
910/915	19·3
Texas crude	13·1
Galician mineral oils—	
880/885 pale	10·4 to 13·2
900/905 ,,	6·1
915 ,,	8·9
Roumanian residuum	17·8
Russian mineral oils—	
895 spindle	2·6 to 3·0
907 engine	3·0 to 8·5
912/915 red cylinder	10·0
Kerosene residuum	6·9
Scotch mineral oils—	
860/868	28·8 to 41·6
880/885	20·2 to 22·2
Neatsfoot oil, English	58·4 to 63·2
,, ,, filtered	70·6 to 75·1
,, N. American	60·7 to 71
,, ,, filtered	70·6 to 71
,, S. American, filtered	69·1 to 72·6
Neutral wool fat	19·7 to 22·7
95/100 per cent. Oleines—	
Australian white, distilled	77·9 to 79·6
American ,, ,,	82·1 to 113·3
,, brown, ,,	76·8 to 110
Belgian white, ,,	82·7 to 84·4
,, brown, ,,	80·5 to 87·7
,, white, saponified	69·5
,, brown, ,,	66·4
Cotton brown, distilled	83·4 to 99·5
Dutch white, ,,	82·2
,, brown, ,,	82·3 to 86·1
English white, ,,	84·7
95/100 per cent. Oleines—	
English brown, distilled	83·4 to 84·4
French white, ,,	84·4
,, brown, ,,	78·3 to 88·9
Fish brown, saponified	138·5 to 153·8
,, distilled	86·1 to 97
Spanish brown, saponified	80
Soya bean brown, saponified	120·4
Recovered oleines, 40%	51·7 to 56·5
,, ,, 45%	54·4
,, ,, 50%	57·2 to 58·8
,, ,, 55%	65·7
,, ,, 60%	60·2 to 65·9
,, ,, 65%	52·5 to 62·8
,, ,, 70%	62·4
,, ,, 80%	66·0
,, ,, French 50%	61·2 to 61·6
,, ,, cotton 50/55% filtered	68·7
,, ,, cotton 70/75% filtered	72·6 to 79·9
Olive oil, Algerian	82·3 to 85·6
,, Candia	79·8 to 88·3
,, Gallipoli	78
,, Malaga	82 to 86·5
,, Pharma	85·6 to 85·9
,, Seville	83·6
,, Smyrna	83·2
,, Substitutes	59·9 to 94·7
Palm oil	51·4 to 53·8
,, bleached	51·1
Paraffin wax, Scotch, 110/112 M.P.	10·5
,, ,, 118/120 M.P.	4·9
,, ,, 120/127 M.P.	3·3
,, American, 106/108 M.P.	5·4
,, ,, 120/122 M.P.	1·9
,, ,, 135/140 M.P.	1·0
,, ,, 130 yellow scale	3·5
Petroleum jelly, white	5·7 to 8·1
,, ,, yellow	9·1 to 11·3
Pitches, mineral oil, Pennsylvania, 180 M.P.	42·7
,, ,, Kansas	31·2
,, ,, Russian, 150 M.P.	56·1
,, wool grease, English	29·6 to 45·2
,, ,, French	38·1
Rape oil, Black Sea, crude	110·3
,, ,, refined	103·6 to 114·3
,, East India, ,,	101 to 107·5
,, German	99·5
,, Jamba	102

TABLE OF IODINE VALUES—*continued.*

Resin, American K	200·2
,, French K	223·8
,, ,, WW	228·6
,, Greek	222·5
Liquid resin	145·7
Resin oil, pale neutral	84·2
,, ,, refined	27 to 60·1
,, dark ,,	63·8
,, ,, sweet refined	52·9
,, grease making	77·4
,, ,, strong	59·7
Rice oil, English	96·6 to 107·9
Salmon oil, Californian	146·2
Sea elephant oil	117·4 to 120·6
Seal oil, water white	147·9
,, straw	124·4 to 142·5
Seconds from hard grease distillation	39·8 to 41·7
Shark liver oil, refined	106·4
Spirit oil from grease distillation	56·6
Soya bean oil, English refined	116·2 to 136·1
,, ,, Manchurian refined	136·3
Sulphonated oils, 70% castor	53·7 to 58·1
,, ,, 50% ,,	34
,, ,, 25% ,,	19·1
,, ,, 50% maize	33·3
,, ,, 50% seal	46·4
,, ,, dark soluble leather oils	52·1 to 80·8
,, ,, pale soluble leather oils	28·2
,, ,, monopol oil	47·1
,, ,, ,, soap	46·8
Sperm oil, Arctic	72·4 to 84·8
,, Southern	79·8 to 80·3
Stearine candle, 122 M.P.	23·4
,, ,, 130/135 M.P.	9·4 to 14·8
,, recovered, white, from black oil, 115 M.P.	25·1 to 28·7
Stearine, recovered, pale, 100 M.P.	24·4 to 38·9
,, ,, ,, 100/105 M.P. from black oil	32·9 to 34·3
,, ,, ,, 110 M.P.	26·8 to 31·4
,, ,, ,, 110 M.P., cotton	91·9
,, ,, ,, 110/115 M.P.	23·9
,, ,, 120/125 M.P. pale, from greases	12·2
,, ,, 120/125 M.P. yellow	29·8 to 31·8
,, ,, 130/135 M.P. pale	11·2 to 21·4
,, ,, 130/135 yellow	17·7
,, ,, 140/145 M.P. cholesterine wax	34·4 to 41·4
Tallow mutton	39·4
,, ,, No. 2	48·6
,, beef No. 2	51·4
Tea seed oil, refined	84·1 to 84·7
Tung oil	158·7
Unsap. from 60% black oil	33·4
,, hard grease	47·4
,, 65% distillate	63·9
,, 75% ,,	71·5
,, 50% ,,	67·7
,, 70% oleine	68·3
,, 60% ,,	62·4
,, 50% ,,	67·9
,, neutral wool fat	32·1
,, 100/105 M.P. pale stearine	47·2 to 49·8
Walnut oil	128·3
Whale oil No. 0	105·8 to 133·4
,, No. 1	119·7
,, No. 2	108·7 to 126·2
,, No. 3	114·8
,, No. 4	124·5

SAPONIFICATION VALUE.

The saponification value of an oil or fat is the number of milligrammes of caustic potash required to saponify 1 gramme of the oil or fat; this figure is of course ten times the percentage of potash required to saponify the sample, and in commercial work the percentage of potash is the figure generally required.

Two to three grammes of the sample (not more) are weighed into a resistant glass flask, 25 c.c. of approximately N/1 alcoholic potash added, and boiled for thirty minutes under a reflux condenser. After cooling, the contents of the flask are back titrated with N/2 hydrochloric acid, using phenolphthalein as indicator. A blank test must be made with each batch of tests started, the number of cubic centimetres of acid used for the back titration is subtracted from the number of cubic centimetres required for the blank, then the difference multiplied by 0·2805 and divided by the weight of the sample taken gives the saponification value of the sample.

Sample.	Saponification Values.
Animal oil, pale	196 to 198
,, ,, brown	195
Arachis oil, refined	193
Black oil, recovered	119 to 198
,, ,, ,, extracted	36 to 45
Blown East India rape oil	188 to 213
,, Black Sea rape (ravison)	214
,, cotton oil	215
,, whale oil	214
Boiled linseed oil	184 to 188
,, ,, substitutes	80 to 98
Bone fat	196
Castor oil, firsts	176 to 183
,, ,, seconds	182
Colza oil, Stettin	169 to 178
,, ,,	178
Cocoanut oil, pressed	264
Cameline oil, refined	189
Cod oil, British crude	170
,, ,, ,, tanked	180
,, ,, Japanese	187
,, ,, Newfoundland	187
Recovered grease distillates 80 per cent.	168
,, ,, ,, 70 per cent.	144 to 148
Fish stearine, pale	197
,, ,, brown	198
Recovered grease, soft, under 20 per cent. unsap.	160 to 180
Recovered grease, medium, under 28 per cent. unsap.	150 to 160
Recovered grease, hard, over 28 per cent. unsap.	91 to 130
Japan fish oil	184 to 185
Lard oil, extra	192 to 198
,, ,, prime	197 to 201
,, ,, brown	199
Linseed oil, Baltic	188 to 191
,, ,, Canadian	192
Menhaden oil, brown	185 to 189
Neatsfoot oil, filtered	188 to 198
,, ,, unfiltered	194 to 198
,, ,, American	193 to 204
95/100% oleines, American brown	194 to 200
,, ,, Belgian white	196
,, ,, English brown	180 to 195
,, ,, French white	205
,, ,, ,, brown	204
Recovered oleines, 70 per cent. saponifiable	152
,, ,, 65 per cent. saponifiable	146
,, ,, 60 per cent. saponifiable	147
,, ,, 55 per cent. saponifiable	157
,, ,, 50 per cent. saponifiable	116
,, ,, 45 per cent. saponifiable	104
Olive oil, Algerian	182 to 198
,, ,, Candia	188 to 198
,, ,, Gallipoli	186 to 195
,, ,, Malaga	186 to 193
,, ,, Seville	187
,, ,, Smyrna	195
,, ,, Sulphur	194 to 213
,, ,, Substitute	164
Palm oil	201 to 215
,, ,, bleached	202
Rape oil, Black Sea (ravison)	179
,, ,, East India, refined	169 to 177
,, ,, Jamba	162
Sardine oil	193
Seal oil, white	196
Sea elephant oil	188 to 194
Sperm oil, Arctic	111 to 139
,, ,, Southern	120 to 138
Soya bean oil, refined	191 to 197
Recovered stearines, pale 100/105 M.P.	160 to 195
,, ,, pale 110/112 M.P.	165
,, ,, pale 120/122 M.P.	121
,, ,, pale 130/135 M.P.	130
,, ,, yellow pale 135/140 M.P.	154
Tung oil	197
Tallow beef	193
Walnut oil, refined	185
Walrus oil, refined	195
Whale oil, No. 1	195
,, ,, ,, 2	184 to 195
,, ,, ,, 3	196

DETERMINATION OF VOLATILE FATTY ACIDS.

The Reichert-Meissl value is usually taken as the measure of the amount of volatile fatty acids present in a sample, but, at the best, it only accounts for 80 per cent. of the total present.

Reichert-Meissl Value.—Take a flask of about 300 c.c. capacity and weigh into it 5 grammes as near as possible of the sample, add 2 grammes of stick caustic potash and 25 c.c. of alcohol, fit flask with reflux tube, and boil the contents for thirty minutes. The flask is now uncoupled from the reflux and heated on the steam bath until all the alcohol has evaporated off (this is most important). Add 132 c.c. of distilled water to the contents of the flask, and warm until the soap is completely dissolved. Then add 8 c.c. of sulphuric acid (made by mixing one part of concentrated sulphuric acid and four parts of water, both by volume), next add two or three pieces of pumice about pea size. The flask is now coupled to a bulb tube, to prevent spirting, and to a condenser, and the contents of the flask warmed until the fatty layer is clear, and then boiled until 110 c.c. have distilled over. The distillation should be completed in about thirty minutes. The distillate is now mixed and filtered through a dry filter paper, rejecting the first 10 c.c. that comes through. 100 c.c. of the filtrate are titrated with N/10 caustic potash, using phenolphthalein as indicator. Increase the number of cubic centimetres of N/10 alkali required by 1/10 (to allow for the 10 c.c. of the distillate not titrated). The number of cubic centimetres of N/10 alkali which would have been required if exactly 5 grammes of the sample had been taken is now calculated. The result is the Reichert-Meissl value of the sample.

Recovered greases over 28 per cent. unsap. . .	3·9 to 5·94
Neutral wool fat	5·21 to 5·79
Pressed black oil	1·71 to 3·39

If the determination of the whole of the volatile fatty acids present in the sample is required, the process is carried out like the Reichert-Meissl, so far as the saponification, evaporation, and decomposition of the soap. Then the distillation flask must be coupled to a flask or can for generating steam; the steam is blown into the distilling flask, and the distillation continued until 100 c.c. of the filtered distillate do not require more than 0·1 c.c. of N/10 alkali for neutralisation.

TOTAL INSOLUBLE FATTY ACIDS.

The Hehner value has no meaning except in the case of fatty oils containing practically no alcohols except glycerol and free from other unsaponifiable matter. With many commercial products this determination is only fatty acids plus unsaponifiable matter, unless one extracts the soap solution with ether or petrol first.

Hehner Value.—Saponify 4 grammes of the sample with approximately N/1 alcoholic potash, and evaporate to a paste. Then dissolve the soap in water and wash into a weighed beaker, using in all 400 c.c. of water, add excess of hydrochloric acid, and heat until the fatty acids have collected into a clear layer on the surface (in the case of liquid bodies 5 grammes of paraffin wax must be added in order to provide a solid cake when cold), cool thoroughly, pour the aqueous liquor through a filter, and wash the cake with cold water without removing it from the beaker. Stir up the fatty acids in the beaker with 250 c.c. of hot water, cool thoroughly, filter, and wash the cake again. Repeat this treatment three times. After a final thorough washing with cold water, place the beaker containing the fatty acids beneath the funnel, and dissolve any fatty acids which the filter carries by washing the filter with absolute alcohol, allowing the alcohol to run into the beaker containing the fatty acids, evaporate off the alcohol, and dry to constant weight in the water oven.

The above is not the original method of Hehner, and usually gives results higher by 1 to 2 per cent. than the original. The washing of the fatty acids on the filter, which was the original method of Hehner, so very often resulted in globules of fatty acids being found in the filtrate, that any means of avoiding this washing is to be welcomed. The process as given above is that used by the Government laboratory at Somerset House. The chief value of the above process is in detecting the addition of oils containing a fair percentage of volatile fatty acids, such as dolphin or porpoise oils, say, in crude whale. It will be found useful to check all marine animal and fish oils in this way at regular intervals.

MACKEY'S OIL TESTER.

This and the heating test with sulphuric acid are the quickest means we have for deciding as to the safety (for insurance purposes) of oils used in the textile trades.

The Mackey tester may be procured from Reynold's & Branson of Leeds, and full instructions are given with the apparatus.

TABLE OF RESULTS OBTAINED WITH MACKEY TESTER.

Oil.	Temperature F. in one Hour.	
American, 95 per cent. brown Oleine	210	300 in 75 minutes
,, ,, ,, ,, ,,	300 in 50 minutes	
,, ,, ,, ,, ,,	209	300 in 75 minutes
,, ,, ,, ,, ,,	207	300 ,, 80 ,,
,, ,, ,, ,, ,,	210	216 ,, 2 hours
,, ,, ,, white ,,	201	215 ,, ,, ,,
Australian, ,, ,, ,, ,,	205	208 ,, ,, ,,
Belgian, ,, ,, brown ,,	200	206 ,, ,, ,,
Cotton oil, refined	300 in 55 minutes	
English brown, 95 per cent. Oleine	213	300 in 80 minutes
,, ,, ,, ,, ,,	200	202 in 2 hours
,, ,, ,, ,, ,,	203	209 ,, ,, ,,
,, pale ,, ,, ,,	203	300 in 101 minutes
,, ,, ,, ,, ,,	205	300 ,, 75 ,,
Fish oil fatty acids	300 in 35 minutes	
French brown, 95 per cent. Oleine	188	206 in 2 hours
,, pale ,, ,, ,,	204	235 ,, ,, ,,
9 olive oil, 1 seal oil	203	215 ,, ,, ,,
Olive oil, substitute	240	300 in 82 minutes
,, ,, ,,	255	300 ,, 63 ,,
Sea Elephant oil	280	300 ,, 65 ,,
Seal oil, white	300 in 48 minutes	
Soya Bean oil, refined	220	300 in 89 minutes
Whale oil, white	300 in 37 minutes	
Cotton Oleine, 70 per cent.	204	300 in 2 hours
Wool grease Oleine, ,, ,,	205	300 in 95 minutes
,, ,, ,, ,, ,,	225	300 ,, 80 ,,
,, ,, ,, ,, ,,	204	300 ,, 94 ,,
,, ,, ,, ,, ,,	205	215 in 2 hours
,, ,, ,, ,, ,,	203	217 ,, ,, ,,
,, ,, ,, ,, ,,	201	300 in 90 minutes
,, ,, ,, ,, ,,	198	300 ,, 90 ,,
,, ,, ,, ,, ,,	207	300 ,, 79 ,,
,, ,, ,, 63 ,,	201	206 in 2 hours
,, ,, ,, 40 ,,	204	207 ,, ,, ,,

SPECIFIC TEMPERATURE REACTION.

This is the form given to the Maumené test by Ballantyne and Thomson. Originally Maumené took 50 c.c. of oil, added 10 c.c. of concentrated sulphuric acid, and stirred with a thermometer until the mercury ceased rising and the highest point reached was read off, then the highest point reached minus the original temperature of the oil and acid gives the Maumené value of the sample.

It was found later that a difference of 2 or 3 per cent. in the acid content of the sulphuric acid used made a considerable difference to the results. Thomson and Ballantyne found that if a blank test was made, using water instead of oil, and the rise obtained with water divided into the rise with oil and the result multiplied by 100, the difference in the test of the acid used did not affect the result, which they called the specific temperature reaction.

The proposal to add mineral oil with a known test to keep down the high rise given by drying and fish oils is of no value, but an actual hindrance when examining mixtures.

Although this test has had ridicule heaped upon it because it is only supposed to give in a poor way the information given with accuracy by the iodine value, it really gives information in one operation, and that only a short one, which the iodine value of the same sample would not give a trace of. Take the case of mixtures containing drying or semi-drying oils. A mixture had an iodine value of 62·3, had no bloom to indicate mineral oil, contained no dinitro-naphthalene, and yielded no yellow colouring matter to alcohol, and therefore contained no debloomed mineral oil, so that the iodine value 62·3 would not lead one to suspect the presence of semi-drying oils; nevertheless, the sample had a specific temperature reaction of 106, which gives immediate indication of semi-drying oils.

TABLE OF VALUES OBTAINED WITH BALLANTYNE AND THOMSON'S METHOD.

OIL.	SPECIFIC TEMPERATURE REACTION.	OIL.	SPECIFIC TEMPERATURE REACTION.
	Degrees F.		Degrees F.
American, 95% Oleine white	102	English, 95% Oleine sap. brown . .	100
,, ,, Oleine brown	109 to 133	French, 95% Oleine brown . . .	107
,, ,, Oleine brown	97	Olive oil . . .	91
Australian, 95% Oleine white . . .	75	,, ,, substitute .	106 to 117
Belgian, 95% Oleine white	107	Rape oil, East India, refined . . .	113
,, ,, Oleine brown	96	Ravison, refined . .	117
Cotton oil, refined .	164	Seal oil, white . .	185
Dutch, 95% Oleine white	88	Soya Bean oil, refined .	173
English, 95% Oleine white . . .	126	Wool grease Oleines, genuine . . .	82 to 90
		Wool grease Oleines containing resin .	132 to 145

To gain as much information from the iodine value one would have to separate first free fatty acids, then the unsaponifiable matter, and finally the fatty acids of the portion originally present as neutral oil. The iodine value of these last fatty acids would then give the information obtained in a few minutes by the specific temperature reaction. It must not be forgotten that it is not possible to calculate what the specific temperature reaction of a mixture will be from the figures given by the constituent oils. When the analysis of the above mixture was finished its specific temperature reaction calculated from the constituents was only 88 against the actual figure 106. The specific temperature reaction being constitutive and not additive explains why it is of such great value in the examination of mixtures.

The procedure of Thomson and Ballantyne should be followed, and the reaction carried out in a Dewar vacuum tube.

LACTONES.

The presence or absence of lactones is at present without commercial significance, yet their presence makes large errors possible in the determination of the molecular weight of the fatty acids from all products that contain lactones.

Determination.—About 5 grammes of the sample are weighed into a flask, dissolved in absolute alcohol, warming if necessary. When quite cold, phenolphthalein is added, and cold alcoholic potash is run in until the solution is alkaline. The cold solution is then extracted with ether meth. twice, the ether is washed twice with water, run off into a weighed flask, the ether distilled off, and the lactones in the flask dried in the oven and weighed.

Lactones may be determined volumetrically, but those present are not always stearolactone (molecular weight 282), which is the lactone usually calculated to.

PERCENTAGE OF LACTONES.

Wool grease Stearines . .	0·8 to 3·5 per cent.
,, Fatty acids . .	Always present; it is doubtful if a sample of wool grease fatty acids has yet been prepared free from lactones.

Hard Yorkshire Grease.—The total saponifiable matter from a sample of hard Yorkshire grease contained 10·85 per cent. lactones, determined gravimetrically; and the molecular weight of the fatty acids after removing the lactones was 342.

The saponifiable matter from the same sample was heated in the boiling water oven for further periods to determine the rate at which the lactones are formed, and each time the molecular weight of the fatty acids was determined in order to find if possible whether the fatty acids that form the lactones are those of high or low molecular weight. The following figures also give an idea of the accuracy obtainable in such experiments:—

Percentage Saponifiable Matter.	Percentage Loss after Heating for				% Lactones. Grav.	Molecular Weight of Fatty Acids.
	8 Hours.	16 Hours.	24 Hours.	32 Hours.		
64·91	...	...	...	...	10·85	342
64·90	1·11	...	...	...	15·77	372
64·91	1·16	1·40	...	...	17·56	393
64·85	1·20	...	1·54	...	21·16	404
64·96	1·23	...	...	1·58	24·55	431

The lactones require 1 c.c. of N/1 KOH to neutralise 1 gramme. The increase in weight on boiling the lactones with acetic anhydride was 4·4 per cent.

The above experiments show that the y-hydroxy acids from which the lactones are formed are contained amongst the fatty acids of lower molecular weight.

ACETYL VALUE.

Original Process.—About 5 grammes of the sample are boiled in a small round-bottomed flask for thirty minutes with acetic anhydride, using 2 c.c. of anhydride for each gramme of the sample taken. All alcohols present will dissolve completely in the hot acetic anhydride; any floating globules will consist of mineral oils or waxes.

Next add 30 c.c. of water to the contents of the flask, and again heat the flask till the contents boil (to decompose residual acetic anhydride). The whole is now poured on to a wet filter, and washed with hot water until acid free; the filter and oil are placed in a beaker, and dried in the oven to constant weight.

Two grammes of the acetylated sample are weighed into a flask, and the saponifiable value determined in the usual way; this saponifiable value is the acetyl value of the sample.

Sample.	Acetyl Value.
Crude Wool grease	156
,, ,, Unsaponifiable matter . . .	131
50 per cent. recovered black oil	129
,, ,, ,, Unsaponifiable matter .	32
Sperm oil, Unsaponifiable matter	181 to 186

This old process, as given above, has been severely criticised by Lewkowitsch, but if one adopts his process, it still does not give the results that Lewkowitsch claims.

Acetyl Value, Lewkowitsch.—Ten or any other convenient number of grammes are boiled with twice the amount of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser, the solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 to 600 c.c. of boiling water, and heated for half an hour, whilst a slow current of carbon dioxide is passed into the liquid through a finely drawn-out tube reaching nearly to the bottom of the beaker; this is done to prevent bumping. (A small piece of porcelain placed in the bottom of the beaker is quite effective, and certainly more convenient.) The mixture is then allowed to separate into two layers, the water syphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed, as may be ascertained by testing with litmus paper. Prolonged washing beyond a certain limit causes slight dissociation of the acetyl product, which would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter paper in a drying oven to remove water. The whole operation may be carried out quantitatively, and in that case the fatty matter is treated in a fashion similar to the *modus operandi* of the Hehner value. It may be useful to work quantitatively if it is desired to ascertain in the first instance whether a notable amount of glycerides of hydroxy acids be present in an unknown fat.

About 5 grammes of the acetylated product are then saponified by boiling with alcoholic potash, as in the determination of the saponification value. If the distillation process be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash; in case the filtration process be used, the alcoholic potash must be measured exactly. It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat. Next the alcohol is evaporated off and the soap dissolved in water. From this stage the determination is carried out either by (*a*) the distillation process, or (*b*) the filtration process.

(a) *Distillation Process.*—Add dilute sulphuric acid (1 : 10), more than is required to saturate the potash used, and distil the liquid in a current of steam. 600 to 700 c.c. of water are distilled off (as a rule this will be found sufficient), and the last 100 c.c will be found to require no more than 0·1 c.c. decinormal alkali. Then titrate the distillate with decinormal potash, using phenolphthalein as indicator, multiply the number of cubic centimetres by 5·61, and divide by the weight of substance taken; this gives the acetyl value.

(b) *Filtration Process.*—Add to the soap solution a quantity of standardised sulphuric acid exactly corresponding to the amount of alcoholic potash employed and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is of course necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*). Both methods give identical results; the latter requires less time, and will therefore be found more convenient.

The author had a few determinations made by the filtration process of Lewkowitsch with the object of finding out whether there was any chance of being able to determine the amount of castor oil in sulphonated products, but the results were so much at variance with those of Lewkowitsch as to make one think that the supposed improvement introduced by Lewkowitsch is of very doubtful advantage in commercial work, and further, to make one think that our real knowledge of the chemistry of this process is less than rudimentary.

Since in analytical work we can only separate fatty acids, and cannot use the original neutral oil, the following experiments were made on the fatty acids separated from the sample. The sulphonated oils were saponified in the ordinary way with alcoholic potash, and the soap decomposed and the fatty acids taken for the experiments.

Fatty Acids from 70 per cent. Sulphonated Castor Oil. Acetyl Value 96·8.—This was the average of two determinations. The sample was taken from a batch made in the works from castor oil of known purity, and yet Lewkowitsch states that a sulphonated oil giving an acetyl value below 120 is a proof that the oil was not pure castor, and still the oil used was perfectly normal in all its figures.

A second sample was taken from the same bottle, and decomposed with hydrochloric acid instead of saponifying. Its Acetyl Value was 124. This again was the mean of two determinations.

The Acetyl Value of original Castor oil 149·7.

Fatty acids after sulphonation of the same oil with 50 per cent. of sulphuric acid.
„ „ from saponification with alcoholic KOH 70
„ „ „ decomposition with HCl 84·7

Since the acetyl value of the fatty acids varies with the amount of sulphonation, the acetyl value, contrary to the statements of Lewkowitsch, is obviously useless for determining the nature of the fatty matter in sulphonated oils.

The most curious feature is the difference in the results between the two methods of preparing the fatty acids, and this appears to show that the saponification with alcoholic potash does not decompose the sulphonated acids completely.

EXAMINATION OF FATTY ACIDS.

All fatty acids should always be freed from oxidised acids and lactones as far as possible (although in some cases, particularly the fatty acids from blown oils, sod oils, boiled oils, and wool greases and some of their products, this is almost impossible) before proceeding with their examination.

The following estimations are usually sufficient to locate the origin of most samples:—

Melting Point, if solid.
Cold Test, if liquid.
Iodine Value.
Oxidised Acids.
Insoluble Bromides.
Separation of Solid and Liquid Acids.
Molecular Weight.

The melting point and cold test of fatty acids are of doubtful value as indications of purity or otherwise, but are most useful commercially. The candle-maker places the highest value on the sample which has fatty acids that show the highest melting point, because the higher the melting point of the fatty acids the higher the yield of stearine, which of course is much more valuable than oleine. The soap-maker also seeks the sample having the highest possible melting point of fatty acids, because the higher the melting point of the fatty acids the harder his soap will be, for a given percentage of soap present. On the other hand, when examining oleines the sample with the lowest cold test is always to be preferred, because the lower the cold test the better the oleine will withstand the vagaries of our climate without the sample leaving the liquid state.

MELTING POINTS.

Fatty Acids.	Melting Point in Capillary Tube (degrees Fahrenheit).
Cotton oil, refined	104
Olive oil	76·5 to 81
Palm oil	115
Tallow	115
„ oil.	100

COLD TEST.

Fatty Acids.	Cold Test (Fahrenheit).	Fatty Acids.	Cold Test (Fahrenheit).
Arachis oil	65 to 75	Neutral wool fat	100 to 115
Colza oil	50 to 58	Olive oil	56 to 80
Cotton oil	88 to 94	Palm oil	112 to 118
Japan fish oil	61 to 78	Tallow	105 to 113
Lard oil	71 to 83	,, oil	81 to 92
Neatsfoot oil	41 to 88	Whale oil	60 to 83

The large variation in the cold test of the fatty acids is caused by the variation in the cold test of the oils themselves; neatsfoot oil, for example, varies from an oil quite clear even in winter, to one which is quite solid and hard according to whether the oil has been filtered or not.

IODINE VALUE OF FATTY ACIDS.

Commercial Fatty Acids—	Iodine Value.	**Fatty Acids prepared in Laboratory**—	Iodine Value.
Animal oil, pale	63·6	50% Turkey red oil	71·0
Castor oil, firsts	89·1	60% Black oil	60·1
,, seconds	89·1	65% Wool grease distillate	26·7
Cotton oil, refined	106·4 to 111·3	70% ,, ,,	36·9
Fish oil	143·7	Soft Yorkshire grease	57·6
Japan fish oil	123·6	Hard ,,	27·0
Linseed oil	167·7	50% Wool grease oleine	46·7 to 51·2
Maize oil	119·7 to 127·1	47% ,, ,,	47·2
Rape oil	148·9	Pale Recovered stearine, melting point 100/105	26·2 to 29·4
Soya bean oil	124·1 to 141		
Whale oil	107·2 to 135·5		

Oxidised Fatty Acids.—Under this heading are included:—

A. All fatty acids insoluble in ether but soluble in hot absolute alcohol; these are only found in products which have undergone a considerable amount of oxidation.

B. All fatty acids soluble in ether but insoluble in petrol-ether, sp. gr. 0·64, and which may be filtered off in a solid state.

It must be understood that oxidised fatty acids are only found amongst the liquid acids, and that they are found amongst the free fatty acids of the sample. These oxidised fatty acids are not present in stearines, hardened oils, etc. The original method of Fahrion is quite useless for the examination of most commercial products, because the presence of only 4 or 5 per cent. of unsaponifiable matter will lower the percentage of oxidised fatty acids found by anything up to 45 per cent. of the total oxidised acids present; this error is caused by the solubility of the oxidised acids in the petrol solution of the unsaponifiable matter.

Oxidised Acids insoluble in Ether.—These acids are solid bodies of a resinous appearance; as found in degras, they were formerly called degras former; they are found in sod oils and in foots from oils of high iodine value. They are left behind adhering to the separator when soap solutions containing them are decomposed with acid to liberate the fatty acids; the fatty acids are dissolved in ether, the ether washed with water and run off, the acids adhering to the sides of the separator washed again with water, the resinous acids are dissolved off the separator with hot absolute alcohol, the alcohol run into a weighed flask, distilled off, and the residual acids dried and weighed.

SAMPLE.	PERCENTAGE OF ACIDS INSOLUBLE IN ETHER.
Sod oil	7·95 per cent.
Whale oil foots	5·99 ,,
No. 4 Whale oil	0·10 ,,
Blown Whale oil	5·26 ,,

Acids soluble in Ether but insoluble in Petrol-Ether.—Weigh 2 to 3 grammes of the fatty acids into a flask, dissolve in 50 c.c. of petrol-ether, warming if necessary, cool, and allow to stand half an hour, filter through a dried and weighed filter, wash the filter with petrol until fat free, dry the filter, and weigh.

The molecular weight of the fatty acids insoluble in petrol is always decidedly higher than the molecular weight of the normal fatty acids in the same sample. The great effect which these oxidised acids have upon the behaviour of commercial products, even when only present to the extent of 1 to 1·5 per cent., hardly seems to have been recognised up to the present. It has long been known, for example, that some cotton oils make a good coloured soap, while the soap from other samples is much darker, or, in the words of the soap boiler, they "work foxy." This discolouration is due to the presence of oxidised acids in the oil. A large proportion of the dark colour of many commercial products is due to the same cause.

FATTY ACIDS FROM	PERCENTAGE PETROL INSOLUBLE IN ACIDS.	MOLECULAR WEIGHT.
	Per cent.	
Bone fat, extracted	1·14	
American brown cotton soap	4·30	
Black cotton grease	5·65 to 50·74	
Soft Yorkshire grease	3·09	356
Hard Yorkshire grease	7·5	
Sewage grease	2·86 to 5·65	435
Grease from crude glycerine tanks	16·8	328
Skin grease, extracted	1·99	
White oleine, American	0·85	
Recovered oleine, 53 per cent.	2·07	
Recovered oleine, 40 ,,	2·61	333
Sod oil	11·42	
Wool fat fatty acids	18·80	427
No. 4 Whale oil	1·05 to 1·50	
Rape oil foots	34·02	376
Whale fatty acids, commercial	4·93	
Fatty acid pitch	23·21 to 64·44	381 to 518
Back ends from wool grease		
Distillation	6·89	540
Blown Whale oil	13·86	322

When materials containing oxidised fatty acids are distilled, a considerable proportion of the oxidised acids are left behind in the still as pitch. The amount of oxidised fatty acids in black cotton greases is sometimes very high, and the yield of pitch from these greases rises with the percentage of oxidised acids in the grease distilled.

Separation of Liquid Acids as Bromides.—The bromides are thrown down as a precipitate on adding bromine to a solution of the oils or their fatty acids.

Octobromides	are insol. in	Benzol.
Octobromides and Hexabromides . . .	,, ,,	Ether.
Octobromides, Hexabromides, and Tetrabromides	,, ,,	Petrol-Ether.

Both direct bromination of the oils themselves and of the fatty acids separated from the oils have been used, but as the bromides from the fatty acids can be washed clean in much less time than can the bromides from the oils themselves, and similar results are obtained in both cases, the bromination of the fatty acids is to be preferred.

Preparation of Bromides.—About 1 gramme of the fatty acids is weighed into a flask, dissolved in 50 c.c. of the solvent, the solution cooled under the tap, while bromine is dropped in until it is coloured red by excess of bromine. The flask is now corked up and let stand overnight. Next morning the contents of the flask are filtered through a dried and weighed filter, the filter is washed with the solvent until fat free. If there is any difficulty in washing all the precipitate out of the flask it will be found easier to dry the flask and contents, weigh, and add the weight of the precipitate to that of the precipitate on the filter.

Rough separation of Bromides.—In order to obtain the separate percentages, three estimations are necessary:—

1. Bromination of fatty acids in benzol . .	ppt. is octobromides.
2. Bromination of fatty acids in ether . .	ppt. is octobromides and hexabromides.
3. Bromination of fatty acids in petrol-ether .	ppt. is octobromides, hexabromides, and tetrabromides.

It will be found necessary to make all the three estimations, if any idea of the nature of the fatty acids present in the sample is required; for though the iodine value gives the measure of the amount of unsaturated acids present, it gives no information whatever as to the nature of the different acids present. For example:—

Coast Cod oil	Iodine Value	134·8
Newfoundland Cod	,,	153·4

The fatty acids of both were brominated, and gave

	Coast Cod.	Newfoundland Cod.
Mixed octobromides and hexabromides .	42·95 per cent.	30·5 per cent.
Tetrabromides.	21·66 ,, ,,	36·03 ,, ,,

The percentage of octobromides from the Newfoundland cod was 11·5 per cent. The Newfoundland cod, although having the higher iodine value, gives the smallest percentage of mixed octo- and hexabromides.

PERCENTAGE OF MIXED OCTOBROMIDES AND HEXABROMIDES FROM FATTY ACIDS.

Castor oil, seconds	nil	Whale oil Fatty acids, commercial	14·01 per cent.
Crude Scotch Cod oil	39·5 per cent.	English Brown Oleine from fish Fatty acids	nil
Coast Cod oil	42·95 ,,	Whale oil, white filtered	21·8 per cent.
Newfoundland Cod oil	40·13 ,,	Whale oil, No. 3	14·7 ,,
Cotton oil, refined	nil	Blown East India rape oil	nil
Soya Bean oil, refined	nil		

PERCENTAGE OF TETRABROMIDES FROM FATTY ACIDS.

Crude Scotch Cod oil	36·03 per cent.	English Brown Oleine from fish Fatty acids	7·11 per cent.
Newfoundland Cod	18·63 ,,	Blown East India rape oil	nil
Coast Cod	21·66 ,,		
Soya Bean oil	9·5 ,,		

Many attempts have been made to determine the melting point of the insoluble bromides yielded by different oils or their fatty acids, but as in most cases the bromides tested have been mixtures of octo- and hexabromides, the results obtained are of very little value. All that can be said with certainty up to the present is that bromides from fish and marine animal oils blacken and char instead of melting on heating, a fact of great value when endeavouring to determine the presence of fish oils in a sample. It must not be forgotten that even when charring takes place we can only say that fish oils are present, but we are left in the dark as to the presence or absence of vegetable oils. This test has considerable value as a qualitative one as a sorting test in the rapid examination of oleines for textile purposes, showing from what class of material the oleine has been made.

Separation of Solid and Liquid Acids.—The method given below, which is the one recommended by Lewkowitsch, is probably the best for general purposes of the many proposed, and if carefully carried out will be found to give liquid acids with an iodine value as high as the fatty acids from any other method that has been put forward. 3 to 4 grammes of the sample, glycerides or fatty acids, are weighed out and saponified with 50 c.c. of approximately N/1 alcoholic potash in a 300 c.c. flask, add phenolphthalein, acidify with acetic acid, titrate back with alcoholic potash until neutral, and dilute the solution to 100 c.c. with water. 30 c.c. of 10 per cent. aqueous lead acetate solution are diluted with 150 c.c. of water and brought to boiling; this solution is run slowly into the soap solution, shaking constantly, so that the lead soap adheres to the sides of the flask when the solution becomes cold. The flask containing the lead soap is filled to the brim with hot water and allowed to cool down to room temperature. When the supernatant liquor has become clear it is poured on to a filter. As a rule the solution is so clear that no particles of lead soap will be found on the filter, otherwise these particles must be washed back into the flask. The lead soap in the flask is washed thoroughly with boiling water, cooling the hot solution before filtering and causing the lead soap to adhere to the sides of the flask; the last traces of water may be removed from the lead soap with a roll of dry filter paper. It is not advisable to dry the lead salts, as they rapidly absorb oxygen from the air. Next 150 c.c. of ether are added to the lead salts, the flask corked, and shaken repeatedly so as to cause disintegration of the lead salts; the flask is then heated on a water bath under a reflux condenser, with frequent shaking. Lead salts of liquid fatty acids dissolve readily in hot ether conjointly with some portions of the lead salts of solid fatty acids; when the undissolved salts settle out at the bottom of the flask as a fine powder the heating is stopped. The ether solution is allowed to cool down to room temperature and filtered through a folded filter into a separator and the filter and flask washed with cold ether, using three or four washes of 25 to 30 c.c. each. The ethereal solution is next shaken with a mixture of hydrochloric acid and water to decompose the lead salts, the ether dissolving the free fatty acids as they form, the lead chloride settling to the bottom of the separator; after separation has taken place the acid layer is run off, the ether washed with water until acid free, and the ether solution run into a weighed flask. The driving off of the ether and the drying of the fatty acids on the water bath must both be done in an atmosphere of carbon dioxide. If the above be done quickly and carefully, the results are as nearly quantitative as we can get them, and the liquid acids obtained have an iodine value as high as can be obtained by any other method.

Fatty Acids from	Percentage of Liquid Acids.	Iodine Value of Liquid Fatty Acids.
Whale oil	69·17 per cent.	147·2
,, ,, ...	61·39 ,,	140·4
Brown Whale cake	43·80 ,,	108·5
70 per cent. Wool grease distillate . .	51·20 ,,	61·2

Determination of Stearic Acid, Hehner's Method.—Prepare a solution of stearic acid by dissolving about 3 grammes of pure stearic acid in 1 litre of warm methylated alcohol of specific gravity 0·8163 in a stoppered bottle. Immerse the bottle up to the neck in ice water, keep in an ice chest well protected against radiation of heat, and allow to stand in the ice water overnight. After twelve hours, syphon off the mother liquor without removing the bottle from the ice water—by means of a small thistle funnel immersed in the alcoholic solution and covered over with a piece of fine calico—so as to retain the separated stearic acid crystals in the bottle. The funnel is bent twice at right angles, and is best fitted into a suction bottle, so that the clear liquor can be drawn off by means of a filter pump. Half to 1 gramme of the fatty acids under examination if solid, or 5 grammes if liquid, are weighed accurately into a flask and dissolved in 100 c.c. of the above alcoholic stearic acid solution. The flask is placed in ice water overnight, the mixture agitated next morning while the flask is kept in the ice water, and then allowed to stand for at least half an hour in the ice water in order to promote crystallisation.

The alcohol is then filtered off as described above, care being taken to draw off the solution as completely as possible. The residue in the flask is washed three times in succession with 10 c.c. of the alcoholic stearic acid solution, and cooled down to 0° C. The crystals adhering to the calico of the thistle funnel are then washed off with hot alcohol into the flask, the alcohol evaporated off, and the residue dried and weighed. It is advisable to take the melting point of the residual stearic acid; it should not be much below 68·5° C.

As the walls of the flask and also the undissolved crystals retain a small quantity of the alcoholic stearic acid solution, a correction must be made. The correction is 0·005 gramme, which must be deducted from the total weight of the residue. Cases are known where this method fails, but it is the best we have.

Molecular Weight of Fatty Acids.—The molecular weight determination is best carried out in connection with the estimation of the total saponifiable matter; after weighing off the total saponifiable matter it is dissolved in alcohol and titrated with N/4 caustic potash, using phenolphthalein as indicator, then the weight taken divided by the number of cubic centimetres of N/1 alkali required gives the molecular weight of the fatty acids of the sample.

The molecular weights given in the following table were determined before the importance of the oxidised fatty acids was recognised; they still appear to have sufficient value to allow of their inclusion. It must always be remembered, however, that they represent only the figures obtained with aqueous potash for the whole of the fatty acids from the products in question. In the case of most of the fatty oils there is only a small amount of oxidised acids present, and there is therefore not much difference in the molecular weights.

TABLE OF MOLECULAR WEIGHTS OF FATTY ACIDS.

Fatty Acids from	Molecular Weight.	Fatty Acids from	Molecular Weight.
Almond oil, refined	283	Whale oil, No. 00	280
Arachis oil, refined	285 to 288	,, No. 1	296
Colza oil, Stettin, refined	318 to 337	,, No. 2	282 to 288
Cotton oil, filtered	273 to 294	,, crude brown	285 to 288
Cod oil, Coast	302	French Resin "H"	336 to 340
,, Medicinal	298	Greek ,,	319
,, Newfoundland	314	American Resin "H"	331
Castor oil, seconds	313	Soft Recovered greases, 5 to 20	
Herring oil, pale	285	per cent. unsap.	260 to 327
Japan fish oil	287 to 305	Medium Recovered greases, 20	
Lard oil, A1	283 to 285	to 28 per cent. unsap.	266 to 356
,, prime	274	Hard Recovered greases, over	
Linseed oil, American	286	28 per cent. unsap.	298 to 445
,, Baltic	289	Black oils	273 to 330
Maize oil, refined	294	Boiled skin greases	261 to 270
Neatsfoot oil, unfiltered	275	Distillates from Soft greases	262 to 289
Olive oil, Bari	279	,, Medium ,,	284 to 290
,, Mitylene	282	,, Hard ,,	290 to 331
Palm oil	266	,, Black oils	269 to 280
,, bleached	268	Oleines from Soft greases	267 to 280
Rape oil, East India, refined	296 to 318	,, Medium ,,	283 to 286
,, ,, blown	300 to 320	,, Hard ,,	281 to 313
Sardine oil, Japanese	285	,, Black oils	262 to 275
Seal oil, straw	282 to 302	Stearines from Soft greases	272 to 290
Sea Elephant oil	285	,, Medium ,,	274 to 301
Soya Bean oil, refined	317	,, Hard ,,	274 to 327
Sesame oil, French	335	,, Black oils	260 to 278
Tallow	273	Candle Stearines	273 to 288
,, oil, pale	270 to 275	Black Cotton grease	287
,, ,, brown	272 to 278	Candle-makers' 95% Oleines	279

If an accurate determination of molecular weight is required, it is essential that both lactones and oxidised fatty acids be removed as far as possible from the crude mixture of normal fatty acids, oxidised fatty acids, and lactones obtained by decomposing the soap solution left after extracting the unsaponifiable matter contained in the sample. No recovered products, wool greases and their products in particular, are free from these oxidised fatty acids, lactones, or both. If they are not removed, the molecular weights are always too high. The oxidised acids and lactones are removed as previously described. This is the only way to obtain the correct molecular weight for the normal fatty acids of the sample. The very high figures given by Lewkowitsch and others for the molecular weights of wool greases and their products are, for the reasons given above, incorrect, and it is to be hoped that no more figures of this description will be published without saying how they were obtained; for example:—

The crude fatty acids from a sample of hard wool grease gave molecular weight 384; after removing oxidised fatty acids and lactones the molecular weight of the normal fatty acids was found to be 342.

MOLECULAR WEIGHT OF NORMAL FATTY ACIDS.

From		From	
40 per cent. Recovered Oleine . .	309	Black cotton grease . .	292
Saponified Oleine from animal fat .	280	Liquid resin	330
,, ,, Whale oil .	302	Wool fat Fatty acids . .	345
Blown Whale oil	284	White American Oleine . .	287
90 per cent. distillate from Recovered grease	279	Brown ,, ,, . .	281
50 per cent. Recovered Oleine . .	295	Greek resin	340
Whale oil Fatty acids . . .	288	Hard Stearine pitch . .	439
Soft wool pitch	375	Sod oil	258
Rape oil foots	330	Sewage grease . . .	304
Soft Stearine pitch	359	French 95 per cent. Oleines .	281 to 287

UNSAPONIFIABLE MATTER.

The bodies met with during the course of commercial examination of unsaponifiable matter are so many and so varied in their nature that it is quite difficult to set out a scheme of examination that will cover all cases. The main classes are:—

1. Mineral Oils.—Legitimate constituents of lubricants only, but may be found in samples of all classes of material.

2. Resin Oils.—As legitimate constituents in certain classes of solid lubricants and some classes of soluble oils, otherwise as an adulterant.

3. Paraffin Waxes.—As legitimate constituent of curriers' greases and artificial petrol jelly, otherwise an adulterant. The lowest commercial melting point is 102/105° F., which is the melting point of American match wax.

In some cases mixtures of mineral oil and paraffin wax are used; for instance, in curriers' greases, and when extracted together as the unsaponifiable matter of the sample, we obtain mixtures that cannot be distinguished from a petrol jelly.

4. Alcohols.—The unsaponifiable matter from certain waxes, sperm oil, shark liver oil, neutral wool fats, and wool greases consists of mixtures of alcohols, which may be separated from the members of the other classes

almost quantitatively by means of the solubility of the alcohols in acetic anhydride.

5. The Remaining Class is the one which has caused, and is still causing, more trouble than all the others together, but if official limits were fixed, if only provisionally, there would be some definite basis to work upon.

This class is the decomposition products which physically, but not chemically, resemble mineral oils, and are formed of the distillation of oils and fats whose unsaponifiable matter originally existed in the form of alcohols. In very rare cases tar products are found, but their qualitative estimation as original constituents is practically impossible at the present time.

General Examination.—The first test should always be the qualitative test of Hager and Salowski. A small quantity of the isolated unsaponifiable matter is dissolved in a few cubic centimetres of chloroform in a test-tube and an equal volume of concentrated sulphuric acid poured gently down the test-tube side; if cholesterol be present, the chloroform turns blood red. The colour of the chloroform changes to purple on standing.

Isocholesterol.—Place a small quantity of the unsaponifiable in a test-tube, add 20 drops of acetic anhydride and 2 drops of concentrated sulphuric acid; isocholesterol gives a green colouration. This second test is often unnecessary, as the sulphuric acid layer in the cholesterol test is always turned green in the presence of cholesterol.

SPECIFIC GRAVITY OF UNSAPONIFIABLE MATTER AT $\frac{60^\circ}{60}$ F.

From	Specific Gravity.	From	Specific Gravity.
American mineral oils	·850 to ·955	Wool grease oleine, 70% sap.	·9023 to ·9153
Scotch ,, ,,	·865 to ·900	,, ,, 60 ,,	·8944
Russian ,, ,,	·890 to ·917	,, ,, 50 ,,	·9001 to ·9277
Resin oils	·970 to 1·015	Arctic Sperm oil	·8688
American Paraffin wax	·853 to ·882	Pale 110/112 M.P. Stearine (wool grease)	·8861
Scotch ,, ,,	·881 to ·886	,, 110/105 M.P. Stearine (wool grease)	·8790
Petrol jelly	·852 to ·897	60% sap. wool grease containing mineral oil	·9376
Black oil, 60 per cent. sap.	·9045	90/95% Recovered wool grease distillate	·8886
,, 70 ,, ,,	·9109		
Wool grease, 80 per cent. sap.	·9033		
,, 60 ,, ,,	·9449 to ·9787		
,, Oleine, 90% sap.	·8796		

REFRACTIVE INDEX OF UNSAPONIFIABLE MATTER AT 70° F.

From		From	
60 per cent. Black oil	1·4995	70% Recovered grease distillate	1·5033
Genuine 70% wool grease oleine	1·4976	50% ,, ,, ,,	1·5051
,, 60% ,, ,,	1·4919	102 melting point Recovered grease Stearine	1·5134
,, 50% ,, ,,	1·4929 to 1·4967		

SPECIFIC ROTATORY POWER OF UNSAPONIFIABLE MATTER.

From Genuine 70 per cent. wool grease oleine	+21·6
,, 60 ,, ,, ,,	+16·8
,, 50 ,, ,, ,,	+ 9·6

The above figures are given by the unsaponifiable matter extracted from wool grease oleines of known purity, and yet the German customs fix the specific rotation of 18 for that portion of the unsaponifiable which is insoluble in acetic anhydride, and still the whole unsaponifiable from samples of known purity falls a long way short of the limit fixed.

MELTING POINT IN CAPILLARY OF SOLID UNSAPONIFIABLE MATTER.

	° F.
From Recovered grease under 20 per cent. unsap.	103
,, ,, ,, 28 ,, ,,	114 to 116
,, ,, over 28 ,, ,,	92 to 115
Grease extracted from Sud cake	120 to 124
Cotton Stearine, 97° F. melting point	85
Southern Sperm oil	76

COLD TEST OF LIQUID UNSAPONIFIABLE.

	° F.
From Genuine 70 per cent. wool grease oleine	49
,, 60 ,, ,, ,,	46
,, 50 ,, ,, ,,	50

IODINE VALUE OF UNSAPONIFIABLE MATTER.

From Genuine 70 per cent. wool grease Oleine	47·3 to 68·3
,, 60 ,, ,, ,,	62·4
,, 50 ,, ,, ,,	48·2 to 67·9
,, 70 ,, ,, Distillate	63·9 to 71·5
,, 50 ,, ,, ,,	67·7
60 per cent. Black oil	33·4
Recovered grease over 28 per cent. unsap.	47·4
,, Stearine, melting point 100/102° F.	47·2 to 49·8
Neutral wool fat	32 1
50 per cent. Oleine containing Mineral oil	29·3

ACETYL VALUES OF UNSAPONIFIABLE MATTER.

From Wool greases over 28 per cent. unsaponifiable	131 to 156
60 per cent. Black oil	32

Yield of Acetates from Unsaponifiable Matter.—The unsaponifiable matter is boiled for a few minutes with a few cubic centimetres of acetic anhydride, the excess of acetic anhydride is driven off on the boiling water bath, and the acetates heated in the water oven until free from acetic anhydride.

This is only given as a rapid works method, and if it be clearly understood that it only applies to unsaponifiable matter which is not volatile at 212° F., this will be found quite useful in the works.

YIELD OF ACETATES FROM UNSAPONIFIABLE MATTER.

	Per cent.
From Wool greases over 80 per cent. sap.	7·96
,, ,, 70 ,, ,,	6·7 to 10·7
,, extracted from Sud cake	6·8
Arctic sperm oil	11·5 to 36·3
Southern ,,	33·9
50 per cent. Recovered oleine	1·1
Whale fatty acids	2·3 to 18·8
,, ,, saponified oleine	21·42
Seconds from grease distillation	1·36

MELTING POINT OF ACETATES FROM UNSAPONIFIABLE MATTER.

Soft greases under 20 per cent. unsap.	101° F.
Hard ,, over 28 ,, ,,	88 to 110° F.
,, ,, extracted from Sud cake	90° F.

Attempts made to obtain definite acetates by crystallisation of the crude acetates from absolute alcohol gave the following results:—

Acetates from hard grease saponifiables.	
Melting point of crude acetates.	Melting point of acetates after twice cryst. from alcohol.
91° F.	143° F.
89 ,,	146 ,,
96 ,,	137 ,,

Acetates from the unsaponifiables of brown dist. 95% oleine once cryst. from absolute alcohol	M.P. 134° F.
,, ,, of 70 per cent. oleine three times cryst.	,, 133 ,,
,, ,, of 40 ,, ,,	,, 130 ,,
,, another brand of American 95% oleine three times cryst.	,, 131 ,,
,, ,, ,, ,, four ,,	,, 133 ,,
,, ,, ,, , five ,,	,, 134 ,,

For general works practice it will be found very convenient to separate the unsaponifiable matter into acetic anhydride soluble and acetic anhydride insoluble portions. This separation, like many others in fat analysis, is never complete, since it depends on solubility only, and is therefore much influenced by temperature, relative proportions of solvent and solute, and also again very largely by the presence of different amounts of soluble and insoluble in the mixture. The amount of acetic anhydride taken should not exceed ten times the volume of the unsaponifiable matter, and it will generally be found convenient to boil up in the flask in which the unsaponifiable was weighed; after boiling a few minutes the flask containing the mixture is allowed to cool; during cooling the flask must be watched, and as soon as no more mineral oil or wax separates off the top the whole must be poured on to a warm filter, when we have:—

On the Filter.—Mineral oils and waxes, mixtures of these, or resin oils. Wash well with hot water until the washings are acid free; the oils or waxes are now ready for further examination.

In the Filtrate, which contains all the alcohols present in the sample in the form of acetates. The acetic anhydride in excess is next evaporated off on the steam bath, leaving the acetates behind for examination. If desired these acetates may be weighed, boiled up with alcoholic potash, their saponifiable value determined, and the free alcohols can then be shaken out with petrol-ether for further examination in their original condition.

The Phytosterol Acetate Test is used for the detection of vegetable oils or fats in animal oils or fats. The unsaponifiable matter, the weight of which should be about 0·5 gramme, is boiled with 2 or 3 c.c. of acetic anhydride for a few minutes, heated on the water bath until the excess of acetic anhydride is driven off, and the acetates then dissolved in absolute alcohol and crystallised out at least five times, and the melting point of the acetates taken in a capillary tube.

	Melting Point.
Cholesterol Acetate	114 to 115° C.
Phytosterol Acetate	125 to 137° C.

The digitonin process of A. Windhaus may be used for the separation of cholesterol in mixtures of unsaponifiable matter.

Half a gramme of the unsaponifiable matter is dissolved in warm alcohol and a slight excess of a 1 per cent. solution of digitonin added. After standing a few hours the precipitate is collected on a weighed filter, washed first with alcohol and then with ether, dried at 212° F., and weighed. The weight of the precipitate multiplied by 0·25 gives the amount of cholesterol present. The theoretical factor is 0·243, but as the precipitate is slightly soluble in alcohol, the factor 0·25 allows for this solubility.

This process only estimates free cholesterol and not its ethers, so that if one precipitates an alcohol solution of the sample itself one gets the free cholesterol, and then a second estimation on the mixed unsaponifiable from the sample; the difference between the first and second estimation gives the amount of cholesterol present as ethers.

SECTION IV.

FATTY OILS.

We have now accumulated sufficient figures for most of the commercial oils and fats to enable all questions of purity to be settled without any trouble, and what is wanted at the present time is the gathering together of figures for the commercial brands of the various oils and fats. Had not this lack of figures for commercial classes been so acutely felt, the figures which follow would not have been given.

There are at present on the market samples offered as oils which are really nothing but foots, and we have now arrived at such a point that it is not safe to pass any sample of solid or semi-solid fat without at least melting it up to see if it gives a clear fluid when melted and is water free; even then it is impossible to guarantee freedom from non-fatty matter. The extracted oils of the present day are so carefully freed from solvent, that no distinction can be drawn between pressed and extracted oils.

Colour Tests.—These tests are steadily decreasing in value. The nitric acid test for cotton oil was formerly of value, as the brown colouration was given even by heated cotton oil. But since soya oil has come into general use this test will have to be abandoned, for even the palest refined soya oils give a light brown colouration with nitric acid, and extracted soya oil gives as strong a colouration as cotton oil itself. The sulphur test for cotton oil still stands good, and experiments show that the amount of sulphur that is dissolved in the carbon disulphide can be varied within fairly wide limits without affecting the resulting colouration to any great extent.

Sulphur Olive Oils.—These may contain up to 4 to 5 per cent. of free carbon disulphide that can be driven off in the water oven. Carbon disulphide in smaller amount is detected by Macagno's method of distilling with steam and testing the first portions of the distillate with a copper solution. All extracted olive oils, even after refining and deodorising, by heating and blowing low-pressure steam through the warm oil, still contain sufficient free sulphur to allow of their easy detection.

Free Sulphur and Sulphides are detected by placing a globule of mercury or a fragment of copper in the oil; the formation of metallic sulphide is accelerated at 212° F.

Mercaptans are invariably present in commercial extracted oils, and can be detected by means of mercuric chloride added to the aqueous distillate.

Acidity.—The amount of acidity in oils and fats has but little scientific interest, but in commercial work it is the greatest factor in valuing a given sample, and also determines in many cases whether a given sample will or will not be suitable for a given purpose.

In commercial work the acidity of an oil or fat is usually reported as oleic acid and not as acid value.

Lamp Oils.—Fatty oils used for lamp oils; for mixing with mineral oils for lubricating purposes; mixed with cylinder oils, and in mixtures for gas engines, should in no case contain more than 5 per cent. acidity. In fatty oils used for oiling wool a high acidity is no detriment, but is an actual advantage in the scouring which follows. The acidity of fatty oils is usually reduced by heating, but the reduction of acidity after heating falls with rise in the acidity of the original sample.

The following table shows the acidity before and after heating. The heating was the taking of the flash point.

OIL.	ACIDITY BEFORE FLASH.	ACIDITY AFTER FLASH.
	Per cent.	Per cent.
Colza, Stettin	2·48	1·76
,,	2·45	1·77
,,	3·97	2·84
,,	2·71	2·34
,,	2·34	11·78
Cotton, refined	0·71	0·56
,, ,,	1·08	0·95
,, ,,	0·42	0·56
0·82 per cent. refined	0·82	0·82
,, ,,	0·82	0·82
Linseed, boiled	5·98	4·48
Lard oil, American	1·69	0·55
,, ,,	1·09	0·62
Neatsfoot oil	1·11	0·67
Olive oil	38·07	35·25
Rape oil	2·71	1·50
,, Blown	6·40	5·69
Sperm oil, Arctic	2·70	0·80
Tallow oil	15·65	14·81

Acidity.—In all cases this is expressed as oleic acid. As an example of the commercial use of the acidity determination the case of whale oil may be taken. Since the hardening of oils has attained a commercial scale the price of whale oil has risen considerably, and in consequence many whale oils are now offered under misleading grades. Whale oils are graded according to colour and acidity, the colour varying from water white to very dark brown, and the acidity from 0·5 to 67 per cent.

When testing a large number of graded samples it was found that:

In No. 1 whale only one sample was over 2·5 per cent. acidity,
,, 2 ,, two samples ,, 10 ,, ,,
,, 3 ,, ,, ,, ,, 20 ,, ,,

so that the following may be taken as sound limits:

No. 1 whale must not exceed 2·5 per cent. acidity.
,, 2 ,, ,, ,, 10 ,, ,,
,, 3 ,, ,, ,, 20 ,, ,,
,, 4 ,, is anything exceeding 20 ,, ,,

Fish oils for the leather trade must in no case exceed 12 per cent. acidity or there will be risk of the leather spueing.

TABLE OF ACIDITY PERCENTAGES.

Animal oil, pale	4·2 to 25·55
,, brown	12·02 to 30·32
Arachis oil, refined	0·22 to 2·80
Almond oil, ,,	3·1
Bone fat, boiled	19 to 35
,, extracted	19 to 44
,, marrow	18 to 30
Cameline	1·26
Castor, firsts	0·49 to 1·54
,, seconds	2·12 to 7·40
Cocoa butter	1·13
Cocoanut, pressed	0·14
,, Ceylon	1·12
,, Cochin	1·26 to 19·11
Cod oil, brown	8·54 to 15·61
,, Japan pale	2·66
,, ,, brown	1·54 to 5·32
,, Malabar brown	6·35 to 12·69
,, Newfoundland racked	9·52
,, ,, brown	11·58 to 12·6
,, Scotch crude	9·38
Colza, Belgian	1·97 to 3·22
,, English	1·82 to 3·58
,, German	2·49 to 3·5
,, Stettin	1·41 to 4·48
Cotton oil, crude	14·14
,, refined Bombay	0·14 to 1·27
,, ,, Egyptian	0·09 to 0·26
,, edible	nil to 0·42
Dogfish liver, refined	2·12
Fish stearine, pale	0·7 to 1·96
,, yellow	3·36 to 19·74
,, brown	15·96 to 55·70
,, dark	60·62
Herring oil, British pale	4·94
,, ,, brown	5·14
,, ,, dark	11·39 to 33·49
Hempseed oil, crude	0·4 to 1·06
Horse fat	7·98 to 23·41
House grease	7·98 to 23·41
Japan fish, pale	5·99
,, brown	2·62 to 18·68
Kipper oil, British brown	5·15
Lard pressed	0·28 to 0·71
Lard oil, A1	1·49 to 1·69
,, prime white	3·72
,, prime	1·69 to 5·72
,, extra winter strained	2·38 to 5·60
Linseed oil, American	1·41
,, Baltic	0·51 to 2·43
,, Calcutta	0·57 to 0·61
,, Canadian	0·8 to 2·12
,, Plate	1·41
,, boiled	2·54 to 5·98
Maize oil, refined	0·40
Menhaden oil, pale	4·23
,, brown	3·64 to 5·88
Niger seed, refined	1·08
Neatsfoot oil, pale unfiltered	2·47 to 7·19
Neatsfoot oil, pale filtered	1·96 to 7·40
,, ,, American	0·71 to 13·54
Olive oil, Algerian	2·52 to 13·72
,, Bari salad	1·35
,, Candia	3·78 to 32·43
,, Gallipoli	12 to 33·14
,, Gioja	7·47
,, Levant	14·0
,, Malaga	1·82 to 20·59
,, Mitylene	5·96
,, Pharma	2·39 to 4·62
,, Smyrna	6·72 to 11·63
,, Seville	3·78 to 7·76
,, Sulphur	53·48 to 56·05
Palm oil	24·68 to 56·05
,, Lagos	14·1
,, bleached	14·1 to 27·49
Pilchard oil, brown	7·7
Rape oil, Black Sea, crude	18·68 to 20·45
,, ,, refined	1·82 to 4·34
,, East India, refined	1·26 to 4·24
,, German	1·76
,, Jamba	1·68
Rice oil, British	75·79 to 77·55
Salmon oil, Californian	5·88 to 10·08
Sardine oil, brown	4·79 to 8·81
Sea Elephant oil, No. 1	0·56 to 3·53
,, ,, No. 2	1·41 to 2·82
Seal oil, water white	0·21 to 0·84
,, straw	0·28 to 9·17
,, brown	13·04
,, ,, filtered	6·16 to 6·86
Sesame oil, French	1·85
Shark liver oil, refined	0·71 to 0·81
Sod oil	7·76 to 21·86
Soya oil, crude	33·84 to 35·96
,, refined	0·35 to 5·18
Sperm oil, Arctic No. 1	0·56
,, ,, No. 2	0·42 to 4·34
,, Southern	0·7 to 2·86
Sunflower seed oil, refined	0·81
Tallow	1·55 to 43·71
,, pressed Oleo Stearine	0·28 to 1·80
Tallow oil, fine pale	8·11 to 10·50
,, pale sweet	7·73
,, fine brown	14·21
Tea seed oil, refined	2·12 to 3·53
Tung oil	3·50
Walnut oil, refined	1·83
Walrus oil, refined	1·41
Whale oil, superfine	0·14
,, No. 1 filtered	0·41 to 7·36
,, No. 1 unfiltered	0·71 to 1·61
,, No. 2 filtered	22·31
,, No. 2 unfiltered	0·56 to 11·99
,, No. 3 filtered	10·58
,, No. 3 unfiltered	0·40 to 28·20
,, No. 4	7·76 to 61·69
,, brown filtered	11·63 to 20·09
,, brown unfiltered	7·40 to 55·70

Oil.	Specific Gravity $\frac{60}{60}$° F.	Acidity Expressed as Oleic Acid.	Iodine Value.	Saponification Value.	Viscosity at				Unsaponifiable.	Cold Test of Fatty Acids. ° F.	Mol. Wt. of Fatty Acids.	Refractive Index at 70° F.
					70° F.	140° F.	180° F.	212° F.				
Animal, Pale.	·9123– ·9157	4·20– 25·38	61·3– 63·6	191– 196	306– 412	85– 88	55– 60	44– 50	1·18– 1·60	...	...	1·4650– 1·4710
Animal, Brown.	·9136– ·9141	12·02– 30·32	63·3	195	310	82						
Arachis, Refined.	·9193– ·9197	3·10– 4·94	102·6	...	...	...	...	...	1·30	38	283	1·4705– 1·4745
Bone Fat, Boiled.	·9260	19·04– 29·61	52·9	...	...	...	...	...	0·5– 1·14	Titre 35·4– 37·9° C.		
Bone Fat, Extracted.	·9228– ·9247	18·68– 43·36	54·6– 58·3	...	...	...	...	...	0·85– 3·91	Titre 38– 42° C.		
Bone Fat, Marrow.	·9165– ·9186	17·97– 29·61	...	...	...	...	...	...	0·3– 0·61	Titre 38– 40·5° C.		
Refined Cameline (Dodder).	·9248	1·26	155·5	189	...	...	...	...	...	...	...	1·4794
Castor, Firsts.	·9610– ·9648	0·49– 2·11	83·2– 86·7	176– 186	3861	312– 366	126– 163	78– 112	0·35– 3·26	19– 35	298– 306	1·4794– 1·4803
Castor, Firsts, Calcutta.	·9632	2·82	...	...	...	...	...	...	0·66	...	...	1·4794

Castor, Seconds.	·9586–·9638	2·12–7·40	84·7–86·5	182	...	288–367	118–163	72–90	0·18–1·51	...	313	1·4783–1·4803
Castor, Seconds, Calcutta.	·9632–·9640	2·82	...	...	...	...	...	...	0·78–1·15	...	...	1·4783–1·4784
Castor, Bombay.	·9632	2·82–8·81	...	...	...	...	...	...	0·36–0·66	...	...	1·4794
Chinese Vegetable Tallow.	·9490	5·28										
Cocoanut, Ceylon.	·9213–·9250	1·12–19·11	10·4	...	230	60	44	38	0·33–0·45	...	...	1·4566
Cocoanut, Cochin.	·9361	1·26–2·73										
Cocoanut, Continental.	...	13·16										
Cocoanut, Pressed.	·9256	0·14	8·6	264	...	...	...	...	0·38			
Cocoanut, off Colour.	...	80·02										
Cod Liver, Brown, British Crude.	·9234	11·9	147·2	170								
Cod Liver, Brown, British Tanked.	·9254	12·38	159	180								

OIL.	SPECIFIC GRAVITY $\frac{60}{60}$° F.	ACIDITY EXPRESSED AS OLEIC ACID.	IODINE VALUE.	SAPONIFICATION VALUE.	VISCOSITY AT				UNSAPONIFIABLE.	COLD TEST OF FATTY ACIDS. ° F.	MOL. WT. OF FATTY ACIDS.	REFRACTIVE INDEX AT 70° F.
					70° F.	140° F.	180° F.	212° F.				
Cod Liver, Brown, Coast.	·9254–·9271	8·54–15·61	134·8–157·4	...	...	...	...	...	3·41	...	302	1·4794–1·4803
Cod Liver, No. 3, Coast.	·9281	12·69	...	...	...	...	...	...	3·14	...	...	1·4800
Cod Liver, Pale, Japan.	...	2·66	147·2	187								
Cod Liver, Brown, Japan.	·9167–·9254	1·01–1 36	147·2	187	...	...	...	...	1·01–1·36			
Cod Liver, Brown, Malabar.	·9313	1·01–7·05	...	...	...	...	...	...	0·71–0·92	...	290	
Cod Liver, Pale, Medicinal.	·9264	0·99	143·3	...	...	...	...	...	1·27	53	298	
Cod Liver, Pale, Newfoundland.	...	...	...	...	...	...	...	...	...	...	...	1·4784
Cod Liver, Brown, Racked, Newfoundland.	·9239	9·52	...	...	...	...	...	...	4·53	...	...	1·4784–1·4794
Cod Liver, Brown, Newfoundland.	·9247–·9258	11·58–12·6	138·4–142	187	...	...	...	...	2·2–2·79	...	314	1·4784–1·4794

Cocoa Butter.	...	1·13	34·9	...	...	...	...	...	1·15	116	276	
Colza, Refined, Belgian.	·9149–·9159	1·97–3·22	103·4	169	366–422	98						
Colza, Refined, English.	·9139	1·82–3·58	...	...	346–390	100						
Colza, Refined, German.	·9136–·9160	2·49–3·50	107·7	178								
Colza, Refined, Stettin.	·9135–·9147	1·41–4·48	103·5–106	169–178	374–425	93–102	61–66	48–50	1·23	...	317–337	1·4735–1·4754
Cotton, Refined, American.	·9197–·9295	0·14–1·06	101·5–107·4	188 198	270–355	84	...	...	0·6–1·77	87–93	273–289	1·4735–1·4745
Cotton, Refined, Bombay.	·9226	0·14	104	...	288	...	...	...	1·27			
Cotton, Crude, Egyptian.	·9202	14·14	...	...	...	...	...	...	1·0–3·22			
Cotton, Brown, Egyptian.	·9172–·9282	8·46–10·43	...	...	...	...	...	...	0·97			
Cotton, Refined, Egyptian.	·9224–·9236	0·09–0·26	104–108·4	192–194	...	...	...	...	1·16–1·95	...	...	1·4725–1·4730
Dog Fish Liver, Pale Refined.	·9315	2·12	...	...	...	...	...	...	2·10	17	287	

OIL.	SPECIFIC GRAVITY 60° F./60	ACIDITY EXPRESSED AS OLEIC ACID.	IODINE VALUE.	SAPONIFICATION VALUE.	VISCOSITY AT 70° F.	VISCOSITY AT 140° F.	VISCOSITY AT 180° F.	VISCOSITY AT 212° F.	UNSAPONIFIABLE.	COLD TEST OF FATTY ACIDS. ° F.	MOL. WT. OF FATTY ACIDS.	REFRACTIVE INDEX AT 70° F.
Fish Stearine, White.	...	0·7–2·12	72·2	197	...	...	...	...	0·46			
Fish Stearine, Yellow.	·9290	3·36–19·74	...	...	...	...	...	...	0·41–0·89			
Fish Stearine, Brown.	·9438	15·96–78·96	58·8	198	...	...	...	...	1·35–2·48			
Fish Stearine, Dark.	...	60·62										
Garbage Grease, American.	·9217–·9250	22·21–43·01	...	...	...	...	...	...	1·89–3·92			
Hempseed, Crude.	·9293–·9318	0·4–1·06	161·8–170	191–193	203	...	...	...	1·28–1·76	...	...	1·4794
Herring, Pale, British.	...	...	...	...	...	...	...	...	...	...	...	1·4813
Herring, Dark, British.	·9271–·9494	5·14–33·49	110·3–117·1	...	...	...	...	...	1·5–2·3	71	285–297	
Horse Fat.	·9201–·9212	7·98–23·41	75·7	...	...	...	...	...	0·86–2·44	91	271	
Japan Fish, Pale.	·9226	5·99	...	...	...	...	...	...	0·89			

Japan Fish, Brown.	·9162–·9258	2·62–18·68	101·9–121·1	184–185	...	...	...	...	0·59–5·70	61–71	292–305	1·4735–1·4764
Kipper, Brown, Cold Drawn.	·9271	5·15	...	...	...	...	...	...	3·25	73	297	
Lard, Pressed.	...	0·28–0·71										
Lard Oil, A1.	·9150–·9158	1·46–1·69	75–76	...	381–403	...	...	...	0·82	71–83	283–285	
Lard Oil, Prime, White.	...	5·72										
Lard Oil, Prime.	·9151–·9170	1·69–2·18	70·6–71	197–206	...	...	...	...	...	. .	...	1·4666–1·4725
Lard Oil, Swift's Extra Winter Strained.	·9153–·9212	0·56–5·60	63·7–74·4	192–198	353	80	...	...	...	...	...	1·4676–1·4686
Lard Oil, Off Colour.	·9153	2·31	67									
Lard Oil, Swift's No. 1 Brown.	·9178	18·67	...	199	...	...	...	...	...	...	...	1·4681
Lard Oil, Swift's No. 2 Brown.	·9179	19·73	...	199	...	...	...	...	...	...	...	1·4686
Linseed, American.	·9319	1·41	...	...	...	...	...	...	1·7	...	286	

OIL.	SPECIFIC GRAVITY $\frac{60}{60}$ ° F.	ACIDITY EXPRESSED AS OLEIC ACID.	IODINE VALUE.	SAPONIFICATION VALUE.	VISCOSITY AT				UNSAPONIFIABLE.	COLD TEST OF FATTY ACIDS. ° F.	MOL. WT. OF FATTY ACIDS.	REFRACTIVE INDEX AT 70° F.
					70° F.	140° F.	180° F.	212° F.				
Linseed, Baltic.	·9311–·9347	0·51–2·43	172–186	188–191	...	...	...	...	1·25	...	289	1·4823
Linseed, Calcutta.	·9325–·9327	0·57–0·61	191–198	171–177	208	...	...	...	1·05–1·34	...	...	1·4813
Linseed, Canadian.	·9344–·9362	0·8–2·12	185–190	192	188	...	...	...	1·35–1·80	...	...	1·4770–1·4810
Linseed, Plate.	·9308–·9338	1·33–1·71	181–194	169–178	...	...	...	...	1·35–2·32			
Maize, Refined.	·9243	0·40	121	...	...	...	...	...	1·10	63	294	1·4715
Menhaden, White.	·9326	4·23	...	...	...	...	...	...	1·14			
Menhaden, Brown.	·9314–·9371	3·64–5·88	165·2–189·6	174–189								
Niger Seed, Refined.	·9251	1·08	...	...	...	...	...	...	1·20	66	286	
Neatsfoot, English, Cold-pressed.	·9149	8·97–13·04	...	194								
Neatsfoot, English, Filtered.	·9137–·9180	1·96–7·40	70·5–75·1	191–199	334–385	79–98	59–63	50–51	...	...	...	1·4695–1·4670

Neatsfoot, English, Unfiltered.	·9133–·9174	2·47–7·19	58·4–63·2	197–211	355–385	100	59	48	...	86	275	1·4676–1·4705
Neatsfoot, North American, Cold-pressed.	·9145–·9153	0·71–0·98	67·8	204	395–446	89	58	45				
Neatsfoot, North American, Swifts.	·9145–·9176	0·30–13·54	69·1–71	190–198	...	88	58	46	...	...	...	1·4686
Neatsfoot, South American.	·9132–·9165	1·03–11·76	72·6	193–199	330	87	...	...	...	...	...	1·4695
Neutral Wool Fat.	·9400–·9636	Nil–3·95	19·7–22·7	59–85	...	...	...	...	35·55–73·60	93–115	394–485	
Olive, Algerian.	·9143–·9180	2·52–13·72	82·3–85·6	182–205	336	86	...	...	...	...	...	1·4690–1·4695
Olive, Bari.	·9166	1·35	83	...	323	...	...	...	...	56	279	
Olive, Candia.	·9135–·9171	3·78–32·43	79·8–88·3	188–198	308–324	84–86	55	50	1·02–1·24	61	...	1·4676–1·4705
Olive, Gallipoli.	·9143–·9155	12·0–33·14	75·5–78·1	189–195	344	...	...	...	...	...	...	1·4695
Olive, Gioja.	·9154	7·47										
Olive, Levant.	·9171	13·75–14·0	...	...	302	...	...	...	...	...	...	1·4690–1·4700

OIL.	SPECIFIC GRAVITY $\frac{60}{60}$ ° F.	ACIDITY EXPRESSED AS OLEIC ACID.	IODINE VALUE.	SAPONIFICATION VALUE.	VISCOSITY AT				UNSAPONIFIABLE.	COLD TEST OF FATTY ACIDS. ° F.	MOL. WT. OF FATTY ACIDS.	REFRACTIVE INDEX AT 70 F.
					70° F.	140° F.	180° F.	212° F.				
Olive, Malaga.	·9145–·9169	1·82–20·59	82–86·5	186–193	312	86	...	...	1·22–1·67	...	...	1·4686–1·4705
Olive, Mitylene.	·9150	5·96	81	...	...	...	...	...	0·57	60	282	
Olive, Pharma.	·9146–·9152	2·38–4·62	85·6–85·9	192–195	...	...	...	...	...	...	...	1·4695
Olive, Seville.	·9160	3·78–7·76	83·6	187								
Olive, Fine Spanish.	·9145	2·82–5·18	...	...	316	. .	...	...	...	...	...	1·4703 1·4705
Olive, Smyrna.	·9145–·9159	6·72–11·63	83·2	195	328	...	...	...	...	...	...	1·4690
Olive, Sulphur.	·9172–·9285	53·48–63·81	75·5–80·4	194–213	...	...	...	...	1·68–6·24			
Palm Kernel.	...	8·1										
Refined Palm Kernel.	...	0·1										
Palm, Lagos.	·9256	14·10	53·8	215								
Pilchard, Brown, British.	·9310	7·7										

Rape, Crude Black Sea, Ravison.	·9227–·9229	18·68–20·45	110·3	...	...	...	...	...	1·00–1·65			
Rape, Refined, Black Sea, Ravison.	·9184–·9212	1·83–4·34	106·3–114·3	179	346–360	89–95	...	...	...	...	...	1·4749–1·4774
Rape, Refined, East India.	·9127–·9166	1·05–4·24	101·9–107·5	169–177	365–410	90–103	...	...	1·16–1·81	...	307	1·4745–1·4754
Rape, Refined, English.	·9174	...	...		371	95	...	...	...	...	...	1·4754
Rape, Refined, German.	·9150	1·76	99·5	171	390	...	63					
Rape, Refined, Jamba.	·9129	1·68	102	162	389	97	...	...	...	...	...	1·4745
Low Rape.	·9163	11·49	...	...	340	...	...	...	...	33		
Rice, English.	·9162–·9206	75·79–77·55	96·6–107·9	...	...	...	...	...	3·95–5·40			
Salmon, Californian.	·9230–·9244	5·88–10·1	146·2	...	...	...	...	...	0·66–1·05	...	...	1·4814
Sardine, Japanese.	·9240–·9356	4·79–8·81	...	193	...	...	...	...	0·67	78	285	
Sea Elephant, No. 1.	·9182–·9262	0·56–7·05	120·6	188–194	...	...	...	...	...	...	285	1·4739–1·4762
Sea Elephant, No. 2.	·9198–·9211	2·12–2·82										

OIL.	SPECIFIC GRAVITY $\frac{60}{60}$° F.	ACIDITY EXPRESSED AS OLEIC ACID.	IODINE VALUE.	SAPONIFICATION VALUE.	VISCOSITY AT				UNSAPONIFIABLE.	COLD TEST OF FATTY ACIDS. ° F.	MOL. WT. OF FATTY ACIDS.	REFRACTIVE INDEX AT 70° F.
					70° F.	140° F.	180° F.	212° F.				
Sea Elephant, No. 3.	·9218	1·41										
Seal, Water White.	·9223–·9272	0·28–0·84	147·9	196	233–298	...	...	...	0·24–1·14	44	302	1·4754–1·4774
Seal, Straw.	·9186–·9252	0·28–9·17	124·4–142·5	196	228–298	...	...	...	0·20–3·20	44	282	1·4745–1·4785
Seal, Brown, Filtered.	·9192–·9200	6·16–12·04	...	...	...	...	...	...	0·72–1·07			
Sesame, French.	·9227	1·85	96·9	...	...	...	...	...	2·98	73	335	
Shark Liver, Pale, Refined.	·9122–·9142	0·71–0·81	109	...	...	...	...	...	16·92	...	...	1·4725
Soya Bean, Crude.	·9144–·9147	33·88–35·96	...	...	...	...	...	...	1·46–1·74	...	...	1·4754
Soya Bean, Brown.	·9274	5·29	...	...	270	75	61	47	1·58			
Soya Bean, Refined.	·9228–·9280	0·49–5·18	116·2–136·1	191–197	240–255	75–83	...	...	0·59–0·94	...	317	1·4754–1·4774
Sperm, Crude.	·8984	3·74	...	...	...	...	...	...	40·5			
Sperm, Arctic, Deod.	·8756–·8861	0·56–4·62	72·4–88·1	115–138	141–187	54–65	42	...	33·15–43·23	35–51	296	1·4600–1·4676

Sperm, Southern.	·8794–·8867	0·7–6·0	79·8–80·3	120–125	142–175	53–61	41–43	37	33·18–34·28	...	...	1·4650–1·4760
No. 2 Southern Sperm.	·8818	5·63	...	...	...	...	...	...	34·28	...	...	1·4650
Sunflower Seed, Refined.	·9259	0·81										
Tallow Mutton.	...	3·41	38·8	...	...	...	...	...	0·95	108–113	275	
Tallow Beef.	·9302	5·15	30·6	193	...	...	...	...	1·10–1·40	106	276	
Mutton Tallow, Patagonia.	...	0·7–1·05										
Tallow Mutton, Australian.	...	3·41	38·8	...	...	...	...	...	0·95	108	275	
Tallow, No. 2.	·9313	3·6–43·71	...	...	...	...	...	...	1·68			
Tallow, Oleo Stearine.	...	0·28–1·36	...	...	...	...	...	...	0·42	124	272	
Tallow Oil, Pale Sweet.	·9155	7·73	60·9	...	...	...	...	...	0·98	85	275	
Tallow Oil, Fine Pale.	·9144–·9226	8·11–14·10	59–62	...	...	...	...	...	1·25–1·65	87	270–272	

Oil.	Specific Gravity $\frac{60}{60}$° F.	Acidity Expressed as Oleic Acid.	Iodine Value.	Saponification Value.	Viscosity at				Unsaponifiable.	Cold Test of Fatty Acids. ° F.	Mol. Wt. of Fatty Acids.	Refractive Index at 70° F.
					70° F.	140° F.	180° F.	212° F.				
Tallow Oil, Brown.	·9123– ·9196	14·21– 17·34	...	...	...	...	...	...	0·55– 1·30	88	276	
Tea Seed, Refined.	·9143– ·9181	2·12– 3·53	84·1– 84·7	193	334	72	...	...	0·91– 0·93	...	...	1·4705– 1·4715
Tung.	·9376	3·5	158·7	197	948	156						
Walrus, Refined.	·9226	1·41	140	195								
Whale, No. 0, Unfiltered.	·9186– ·9228	1·41– 2·8	105·8– 127·1	185– 195	240– 293	66– 75	50	42	1·06– 2·80	...	...	1·4748– 1·4764
Whale, No. 0, Filtered.	·9200	0·49– 1·68	107·4	184	270	71						
Whale, No. 1, Unfiltered.	...	0·71– 1·61	...	...	...	...	...	...	...	...	...	1·4725– 1·4735
Whale, No. 1, Filtered.	·9211– ·9244	1·06 7·36	...	...	243– 244	76	53	43– 44	0·41– 1·06	...	...	1·4735– 1·4740
Whale, No. 2, Unfiltered.	·9196– ·9263	0·56– 9·87	108·7	...	...	...	...	...	0·51– 0·71	...	...	1·4715

Whale, No. 2, Filtered.	·9205	22·31	126·2	...	...	...	...	...	...	...	...	1·4752
Whale, No. 3, Unfiltered.	·9225– ·9230	5·67– 37	114·8	196	...	...	...	...	0·4– 1·0	...	...	1·4705– 1·4715
Whale, No. 3, Filtered.	·9194– ·9226	6·0– 10·58	...	196	250	...	...	...	0·90	...	...	1·4739
Whale, No. 4, Unfiltered.	·9207	27·85– 71·56	145·3– 148·6	185								
Whale, No. 4, Filtered.												
Whale, Filtered, Brown.	·9230	11·63	...	...	...	...	...	...	0·68			

SECTION V.

MISCIBLE CASTOR OIL.

This is prepared by heating castor oil at 550 to 570° F. until it loses about 5 per cent. of its weight, when it will be found to mix with mineral oils in all proportions, and becomes practically insoluble in alcohol.

GENERAL FIGURES.

Specific gravity	·9550 to ·9720
Acidity as oleic	0·4 to 3 per cent.
Unsaponifiable	0·53 per cent.
Viscosity	387 to 486 at 140° F.
,, ...	160 to 189 at 180° F.
,, ...	108 at 212° F.
Refractive index at 70° F.	1·4784 to 1·4813
Iodine value	79·4

The following are the figures of the original castor oil, along with the figures from the same oil after heating, until the loss in weight was 6 per cent. :—

	Original Oil.	Miscible Oil.
Specific gravity	·9614	·9720
Acidity as oleic	0·56 per cent.	0·42 per cent.
Unsaponifiable . . .	0·57 ,,	0·53 ,,
Iodine value	83·5	79·4
Refractive index at 70° F. .	1·4803	1·4784
Viscosity at 140° F. . .	329	486
,, ,, 180 ,, . .	126	189
,, ,, 212 ,, . .	83	108
Acetyl value	149·6	93·8

BLOWN OILS.

These are prepared by blowing air through the warm oil until the desired specific gravity is reached. The oils most often blown are rape, cotton, ravison, and more recently whale oil has been blown. The rape oil has often been substituted by ravison, but there is also another substitution which can only be detected by a careful comparison of figures calculated to a definite specific gravity.

Blown oils should always have the unsaponifiables estimated, as such oils are sometimes blown to a high specific gravity and then let down again with mineral oil.

A sample offered as blown rape oil showed the following :—

Specific gravity	·9600	Iodine value	65·7	Viscosity	879 at 140° F.
Acidity	4·94%	Saponifiable value	161	Unsaponifiable	18·97%

If unsaponifiable, saponifiable value, or both, had been omitted it would have passed as pure but not blown very far.

On looking over the figures given for blown cotton and rape oils it will be seen that the figures agree very closely with the exception of the cold test of the fatty acids. The percentage of oxidised fatty acids is about the same in both cases, and varies from 23 to 26 per cent.

The following process has been worked out by Marcusson, depending on the difference in the ether solubility of the lead salts of the normal fatty acids soluble in petrol-ether—that is, on the ether solubility of the remaining fatty acids after the oxidised fatty acids have been removed.

In the case of the oils themselves, weigh out about 2 grammes, and of mixtures weigh out about 8 grammes. Saponify as usual, shake out and determine the unsaponifiable, decompose the soap solution with acid and shake out with ether, wash the ether until acid free, run the ether into a weighed flask, distil the ether off, dry, and weigh. Dissolve the fatty acids in 50 c.c. of petrol-ether, let stand, and filter off the oxidised acids. Distil off the petrol, and from the petrol soluble fatty acids prepare the lead soaps as usual, and treat these lead soaps with ether. The lead soaps prepared in this way from blown rape oil leave only traces of insoluble matter when treated with ether. The lead soaps prepared in the same way from blown cotton oil are only partly soluble in ether, and if the portion of the lead soaps insoluble in ether are decomposed with acid and the fatty acids shaken out with ether, these fatty acids have a melting point of 129 to 138° F.

	EAST INDIA RAPE.	RAVISON.	COTTON.
Specific gravity	·9600 to ·9741	·9650 to ·9708	·9672
Acidity	4·68 to 8·12%	5·18 to 7·14%	7·19%
Iodine value	52·2 to 70·1	66	55·9
Viscosity at 140° F.	800 to 1439	748 to 1100	
,, ,, 180 ,,	300 to 590	313 to 455	
,, ,, 212 ,,	168 to 275	250 to 295	
Saponification value	188 to 213	214	215
Refractive index	1·4803 to 1·4855	1·4803 to 1·4813	1·4803
Unsaponifiable	0·76 to 1·65%	0·79%	1·09%
Molecular weight of fatty acids	300 to 320	...	304
Cold test of fatty acids	49° F.	...	96° F.

BLOWN WHALE OIL.

Specific gravity	·9663	Viscosity at 212° F.	134
Acidity	4·23 to 6·70%	Saponifiable value	214
Iodine value	54·8 to 62·8	Refractive index	1·4774 to 1·4801
Viscosity at 140° F.	289 to 375	Unsaponifiable	1·20%
,, ,, 180 ,,	...		

A further examination of the saponifiable matter from a sample of blown whale oil gave the following figures :—

		Molecular Weight.
Fatty acids insoluble in ether	5·26 per cent.	
,, ,, petrol	13·86 ,,	322
,, soluble in ,,	...	284

BOILED LINSEED OIL.

This is one of the most variable oils on the market, and certainly one of the most often adulterated, the chief adulterants being mineral oils and resin oils, or the boiled oil is mixed with one of the boiled oil substitutes described below.

BOILED LINSEED OIL.

Specific gravity	·9370 to ·9541	Open flash	442° F.
Acidity	2·54 to 5·98%	Molecular weight of fatty acids	269 to 273
Iodine value	146 to 165	Refractive index	1·4833 to 1·4850
Unsaponifiable	0·36 to 2·50%		
Saponifiable value	184 to 188		

The percentage of oxidised acids in boiled linseed oil varies with the extent to which the oil has been boiled. Much work will have to be done in this direction before commercial limits can be fixed.

A linseed oil is useless for boiling if it separates mucilage on heating to 400° F., and is also useless for linoleum manufacture.

Laboratory Boiling Trial.—Heat the oil to 400° F. and blow air through for one hour, keeping the oil at 400° F. after the addition of 0·5 per cent. resin and 0·5 per cent. litharge.

Boiled Linseed Substitutes.—In all cases the saponifiable should be estimated as well as the unsaponifiable. In no case must the determination of the percentage of volatile matter at 212° F. be omitted.

The saponifiable is usually a mixture of boiled linseed and resin. A fairly close approximation to the percentage of resin may be obtained by calculating the acidity of the sample to resin, counting on 85 per cent. of free fatty acids as present in most samples of pale resin. The unsaponifiable will be mineral oil, or, rarely, resin oil.

The volatile matter at 212° F. is usually benzolene, and being volatile at 212° F., may be calculated from the loss on heating to that temperature. The exact nature of the unsaponifiable matter is easily determined from its specific gravity and refractive index.

Boiled Oil Substitutes :—

Specific gravity	·907 to ·960	Iodine value	57 to 110
Acidity	2 to 36% as oleic	Saponifiable value	80 to 100
Unsaponifiable	10 to 35%	Refractive index	1·4800 to 1·500
Volatile at 212° F.	15 to 35%	Open flash	80 to 120° F.

Degras, Sod Oil, Average Figures :—

Specific gravity	·9900 to ·9930	Cold test	48 to 52° F.
Acidity	7·76 to 15·16%	Molecular weight of fatty acids	275 to 295
Unsaponifiable	2·15 to 3·52%		
Water	18·31 to 41·66%		

Sod oils are sometimes partly dried and then sold as water free; their colour is almost black. Such a sample gave:—

Specific gravity	·9735	Water	5·06%
Acidity	21·68%	Non-fats	4·49%
Unsaponifiable	1·93%		

The fatty acids from this sample were separated. Of these, part were so highly oxidised as to be insoluble in ether, but soluble in absolute alcohol, solid, and deserving the appellation "resinous."

The sample contained—

7·95 per cent. resinous acids insoluble in ether.
11·42 per cent. acids insoluble in petrol-ether of mol. wt. 469.
82·00 per cent. normal fatty acids soluble in petrol-ether of mol. wt. 258.

Lactones are always formed on heating oxidised fatty acids, and the splitting off of water to form these causes low results. The total of the above analysis shows that oxidation of the fatty acids is taking place at a greater rate than lactone formation.

A mixture of wool grease and fish oil is often sold as degras in this country and America.

Commercial Neutral Degras is neutral wool fat.

American Hog Greases.—These are really a very low quality of lard, and are often dirty, and may contain a considerable amount of water. The acidity of the hog greases rises to 25 per cent.; water content, 4·78 per cent., dirt, 4·22 per cent.; fat, 91·00 per cent.

American House or Garbage Grease gives the following figures:—Specific gravity, ·9217 to ·9250; acidity, 22·0 to 43 per cent.; unsaponifiable, 1·80 to 3·49 per cent.; water, usually below 0·5 per cent., and generally clean. Large quantities of oleine are made from these greases in the United States, and in consequence these greases are not often marketed in any quantity in this country.

Bone and Marrow Fats.—The qualities usually marketed are—

Marrow Fat.
Boiled or Steamed Bone Fat.
Extracted Bone Fat.

It does not follow that the marrow fat is the best for the glycerine maker, although it is the dearest.

	Marrow Fat.	Boiled Bone Fat.	Extracted Bone Fat.
Specific gravity	·9165 to ·9186	·9178 to ·9260	
Acidity	17·9 to 36%	9·8 to 35·25%	43·3%
Unsaponifiable	0·3 to 0·6%	0·24 to 1·9%	
Water	about 1%	0·27 to 2·5%	0·53%
Ash	,, 0·6%	0·2 to 0·85%	
Cold test	70 to 80° F.	61 to 80° F.	80° F.
Iodine value	53 to 56	53 to 56	54 to 58
Titre of Fatty acids	38 to 41° C.	35 to 41° C.	

Hardened Oils.—Up to the present these are very variable, and the same process does not always give the same results, even when working on the same raw material.

IODINE VALUE OF HARDENED OILS.

From Linseed oil . .	21·7 to 78·1	From Castor oil . . .	15·1 to 25
,, Whale oil . .	23·7 to 63·5	,, Cotton oil . . .	11 to 58

The test worked out in Germany for the detection of hardened oils from fish oils will have to be abandoned, because the violet colouration with iodine tincture, supposed to be given by a solution of the sample in a mixture of equal volumes of benzol and xylol containing 1 per cent. of concentrated sulphuric acid, is also given by the following fatty acids:—

Castor, Linseed, Rape, Cotton, Maize, Soya Bean.

The only likely method appears to be the separation of the liquid fatty acids, bromination of these liquid acids, and separation of the bromides. The bromides from marine animal and fish oils char on heating, whilst the bromides from vegetable oils and fats give a definite melting point without any charring.

When hardened, castor oil has still a high acetyl value, 154, and is insoluble in cold alcohol, but dissolves on heating.

Detection of Nickel.—In order to make quite sure, it is necessary to test the sample itself and the ash of the sample also.

Boil out the sample with hydrochloric acid, and add to the acid solution 0·5 gramme dimethyl glyoxine and 5 c.c. of 95 per cent. alcohol; if nickel is present the solution turns yellow, the colouration remains stable. The ash with the dimethyl glyoxine develops a red colour if nickel is present.

Different batches of the same oil treated by the same process may vary in melting point from 69 to 107° F.

The fat carried over with the hydrogen during hardening is of very variable composition, which is only what might be expected considering the difference in raw materials and also in the processes used.

Acidity	34·90 to 90·40%	Oxidised Fatty acids . . .	1·39%
Unsaponifiable . .	0·62 to 14·35%	Molecular weight of Normal Fatty acids	257
Iodine value of unsaponifiable . . .	70·8	Iodine value of Fatty acids . .	13
Cold test . . .	60° F.		

SECTION VI.

CHEMICAL EXAMINATION.

SULPHONATED OILS.

Qualitative Detection.—Place a few cubic centimetres of the sample in a test-tube, and boil up with three times its volume of concentrated hydrochloric acid until the fatty layer is quite clear; the acid layer is then taken away with a pipette, diluted with water, and on barium chloride being added a white precipitate of barium sulphate shows the presence of sulphonated oils in the sample.

Until recently, castor oil was almost the only oil that was sulphonated to any extent. To-day, oils are sulphonated having an iodine value as high as 150. The old methods of analysis which sufficed for castor products are not suitable for sulphonated products made from oils having a high iodine value. When trying the test indicated above, if the oil was from castor or other oil of low iodine value, the layer of fatty acids over the acid layer will be clear and free from suspended dark particles; but if from oils of high iodine value, the layer of fatty acids will be very dark in colour, and contain many charred particles.

In all that follows, those samples which do not char on boiling with hydrochloric acid are given under the heading *Low Iodine value oils*, and the samples which char under *High Iodine value oils.*

Estimation of Water, Low Iodine Value Oils.—Weigh 2 grammes of the sample into a Petri dish with a small glass rod, and dry in the water oven until the difference between two weighings does not exceed 2 milligrammes.

Estimation of Water, High Iodine Value Oils.—These often char and decompose as the water evaporates off; the water in such samples can only be estimated by distillation with xylol.

Total Fat, Low Iodine Value Oils.—Weigh out 5 grammes into a dish and boil with hydrochloric acid, 1 acid and 1 water by volume, until the layer of fat is quite clear, cool, pour into a separator, and extract twice with ether, washing the ether with water until acid free, run the ether into a weighed flask, distil off the ether, dry the fatty acids in the oven, and weigh

Alternative method.—Weigh out into a dish and decompose as before, then add 10 grammes of stearic acid (not paraffin wax); when the whole of the fatty layer is quite clear the dish is allowed to cool, the acid layer poured off, and the cake washed with water; then the cake is melted up with water again, stirred well and allowed to set, and the water poured off. This washing is repeated three times more and the cake dried and weighed.

Total Fat, High Iodine Value Oils.—Weigh 5 grammes into a flask, dissolve in 50 c.c. of pyridine, add hydrochloric acid, and let stand on the warm water bath for at least one hour with frequent shaking. Cool, and wash into a separator with water, add ether and shake, allow to separate, run off the acid liquor, and wash the ether with water until free from both acid and pyridine. The acid liquor is again shaken out with ether and the ether washed. The ether extracts are run into a weighed flask, the ether distilled off, and the fat dried in the oven, cooled, and weighed.

Total Acid.—This process is applicable to all samples.

Boil 5 grammes of the sample with 20 c.c. of strong hydrochloric acid until the fatty layer is quite clear (neglecting charred matter if present). Pour into a separator, dissolve the fat in ether, run the acid layer into a beaker, wash the ether with water until acid free; uniting the washings and the acid liquor, warm the beaker on the water bath until all the ether has evaporated off, heat to boiling, and precipitate with barium chloride. The barium sulphate found is calculated to sulphuric acid.

Free Sulphuric Acid.—Applicable to all samples.

Weigh out 10 grammes of the sample into a separator and shake out three times with saturated brine, unite and titrate with N/10 alkali, and calculate to sulphuric acid. Make a blank test on an equal quantity of the brine, and deduct any acidity found.

Alkali.—It is not uncommon to find both soda and ammonia present in the same sample of sulphonated oil, the soda being added until the sample is nearly neutralised and finished off with ammonia.

Dissolve 10 grammes of the sample in water and titrate with N/2 acid, using methyl orange as indicator. A further 10 grammes are distilled with soda into N/2 acid, and the amount found calculated to ammonia; then acid required for titration minus acid for distillation equals that due to soda. Either present alone are of course determined by titration only.

Before examining the fatty acids from sulphonated products, care must be taken that the sulphonated compounds are completely decomposed; if this be neglected, the fatty acids will only give figures which are far removed from the truth.

Up to the present we are entirely without methods for determining the purity or otherwise of the oil used. It has already been shown (see acetyl value) that no process for determining the acetyl value yet described gives results anywhere near the original oil. Consequently the acetyl value is of no use in this direction. The iodine value is no better. For example:—

Iodine Value of Oil used.	Iodine Value of 50% Sulph. Oil from same.
83·5	34
135	46·4
116	33·3

The only use of the acetyl value in the examination of sulphonated oils from castor oil is to give an idea as to the amount of sulphuric acid used for sulphonation.

Example:—Castor oil, original acetyl value 149·7, Lewkowitsch,
Same after sulphonation with 25 per cent. of sulphuric acid, acetyl value 96·8, Lewkowitsch,
Same after sulphonation with 50 per cent. of sulphuric acid, acetyl value 70, Lewkowitsch.

The fall in the acetyl value being due to the extent to which polymerisation of the oil has taken place, the higher the percentage of acid used for sulphonation, the greater the lowering of the acetyl value.

It must be remembered that this lowering also depends on the length of time the acid is allowed to act on the oil, and on the washing of the oil also.

NEUTRAL WOOL FAT, LANOLINE.

Prepared from wool grease by neutralisation of the free fatty acids, followed by extraction of the neutral fat with solvents. With the exception of one or two well-known makes these neutral fats are very variable in quality.

Neutral wool fat is often quoted as a fat that does not turn rancid, but a sample of *adeps lanæ* had original acidity 1·09 per cent. After keeping in a closed jar for 2½ years the acidity was 5·18 per cent., a gain of acidity 3·89 per cent.

If iron is present as an impurity in a neutral fat the sample is unfit for certain pharmaceutical purposes, and may be best detected as follows:—The neutral fat is rubbed up with an aqueous solution of salicylic acid, when, if iron be present, the paste is discoloured, or in bad cases turned red; such a sample is unfit for ointment making, and yet it may pass the requirements of the Pharmacopœia.

Specific gravity	·9400 to ·9625	Ash	traces to 0·19%
Acidity	nil to 3·45%	Cold test	89 to 104° F.
Iodine value	19·7 to 22·7	,, of Fatty acids	100 to 110° F.
Saponification value	61 to 86	Molecular weight of Fatty acids	394 to 485
Unsaponifiable	35·35 to 61·37%		
Water	0·25 to 25%		

FOOTS FROM FATTY OILS.

Foots of all kinds require very careful sampling if any approach to accuracy of results is needed.

Foots may be simple settlings from any oil or fat, from acid refining (rape, etc.), or from alkaline refining (cotton, sesame, arachis, etc.).

The first thing is to boil up 2 or 3 grammes of the sample with water; the reaction of the water is taken with litmus paper in order to tell from what source the sample has come. The black greases obtained by decomposing cotton mucilage with acid is usually sold on the percentage of bodies it contains which are soluble in carbon disulphide, but, as carbon disulphide dissolves saponifiable, unsaponifiable, and oxidised acids, this method is obviously unfair to everybody but the seller.

The first estimation should always be water, by drying in the oven as usual. In the case of Pâte d'Arachide the ammonia will be driven off along with the water, and if required separately may be determined by direct titration with N/2 acid, using methyl orange as indicator.

Cotton foots, after the water and dirt estimations, must be decomposed with acid and the fat filtered through a filter, the fat and filter being washed with hot water until acid free, then dried and weighed. The analysis from this point on must be made on the fat thus obtained.

Non-Fats.—Weigh out about 5 grammes into a flask, add 50 c.c. of ether meth., and filter into a weighed flask; the filter is washed with ether until fat free, the ether distilled off, and the fat dried and weighed.

The difference between this weight and the weight taken is equal to the non-fats. The above will be found more convenient than trying to weigh the actual non-fats, which sometimes adhere to the flask until it is impossible to get the whole on to the filter paper.

Free Fatty Acids.—Titrate 2· grammes of the sample with N/4 alkali, using phenolphthalein as indicator.

Unsaponifiable Matter.—Saponify 2 grammes and extract with petrol as usual, saving all the washings.

Available Saponifiable Matter.—The soap solution and washings from the unsaponifiable estimation are united, the alcohol evaporated off on the water bath, the remaining solution decomposed with acid, poured into a separator, and shaken out with petrol-ether, washed with water, and filtered into a weighed flask, distilled off, dried, and weighed. This gives the total available saponifiable matter for soap making or for distillation. If the percentage of the oxidised acids is required, proceed as below.

Total Saponifiable Matter.—The soap solution and washings are decomposed with acid and shaken out with ether meth. twice, the ether washed with water until acid free, run into a weighed flask, the ether distilled off, and the fatty acids dried and weighed.

Oxidised Acids.—The fatty acids from the total saponifiable estimation are dissolved in 50 c.c. of petrol-ether, warming if necessary under a reflux tube, allowed to cool, and when cold filtered through a weighed filter; the filter is washed with petrol until fat free, then dried and weighed. The oxidised acids may be dissolved off the filter with absolute alcohol if their molecular weight is required.

Stiepel has proposed to examine foots by Twitchell's process and take the method as a standard; foots have been put on the market, any dispute over which were to be settled by Stiepel in Berlin. It would probably be much better to wait until we know more about these oxidised acids rather than attempt to standardise the estimation of practically unknown bodies.

PÂTE D'ARACHIDE.

Water and ammonia rise up to 12 per cent., but these foots are usually decomposed before being marketed. Test after decomposing:—

Specific gravity	·9262 to ·9315	Unsaponifiable	1·45 to 1·90%
Acidity	23·97 to 45·83%	Cold test	23 to 55° F.

COTTON MUCILAGE.

Water	5 to 56 per cent.
Non-fats	3 to 5 ,,
Soap	up to 40 ,,

BLACK COTTON GREASE.

(These are the so-called American concentrated soap stock.)

Specific gravity	·9197 to ·9825	Unsaponifiable	1·7 to 27%
Water	2 to 20%	Oxidised acids	2·5 to 50%
Non-fats	1·37 to 21%	Molecular weight of Normal Fatty acids	275 to 298
Available saponifiable	14 to 87%		

Rape Oil Foots.

Specific gravity	up to ·9800	Water	up to 20 per cent.
Acidity	2·8 to 62 per cent.	Cold test	up to 55° F.
Unsaponifiable	up to 22 ,,	Non-fats	up to 5 per cent.

The saponifiable matter from a sample of rape oil foots gave the following figures:—

65·89 per cent. normal fatty acids of molecular weight	330
34·02 per cent. oxidised acids of molecular weight	376

Olive Oil Foots

are not often found on the English market, but some of the finest candle stearine obtainable is made in Italy from olive foots.

Specific gravity	·9218 to ·9249	Water	62 to 94 per cent.
Acidity	43·71 to 49·35%	Molecular weight of Fatty acids	271
Unsaponifiable	3·45 to 9·36%		

Whale Oil Foots.

Water	up to 35 per cent.	Unsaponifiable	about 1 per cent.
Non-fats	up to 15 ,,	Acidity	9 per cent. upwards.

Soya Foots.

Acidity	up to 20 per cent.	Water	up to 20 per cent.
Unsaponifiable	0·96 ,,	Non-fats	3 to 24 ,,

Palm Foots.

Specific gravity	·9414	Water	2 to 10 per cent.
Acidity	up to 60 per cent.	Non-fats	up to 38 ,,
Unsaponifiable	22 ,,		

Newfoundland Cod Foots.

Acidity	36 per cent.	Water	12 per cent.
Unsaponifiable	1·10 ,,	Non-fats	17 ,,

Copra Residues.

The colour of the oil contained in these copra residues varies from a full brown to almost white.

Oil	21·39 to 36·89 per cent.	Non-fats	23·06 to 65·79 per cent.
Water	6·04 to 55·64 ,,	Acidity	43·47 to 91·81 ,,

SECTION VII.

FAT SPLITTING.

THE two methods in commercial use at the present time are:

1. Splitting in open vessels at atmospheric pressure.
2. ,, ,, autoclave with high-pressure steam.

1. **Open saponification** with lime is not carried on on a large scale at the present time, the processes in use being the castor seed, the Twitchell and the Pfeilring spalter, both of which make use of naphthaline sulphonic acids or their salts.

The difficulties involved have not yet been entirely overcome with any of these processes.

The castor seed process gives difficulty in the separation of the fatty acids from the glycerine.

The Twitchell process gives slow splitting, and also fatty acids, which are liable to work "foxy" in soap making.

The Pfeilring spalter gives slow splitting, and difficulty in obtaining a marketable crude glycerine.

2. **Autoclave Splitting.**—At the present time the action of the high-pressure steam is always assisted; usually with magnesite, slaked lime, or with zinc oxide.

Even in the autoclave, using at the same time steam pressure and a percentage of alkali, the splitting obtained varies not only with different fats, but with different batches of the same fat. A minimum of 90 per cent. decomposition should always be aimed for, though there are fatty acids placed on the market which are below 90 per cent. It need hardly be stated that all autoclave samples should be decomposed before testing. This is done by boiling up with 25 per cent. sulphuric acid until the fat layer is quite clear and free from emulsion underneath; the acid is syphoned off, and the fatty acids washed four times with hot water, syphoning off the water each time, then 2 grammes of the fatty acids are titrated with N/4 alkali, and calculated to oleic acid.

All autoclave fatty acids after decomposing should be tested to make sure that the sample is free from insoluble soaps (this test should also never be omitted when testing commercial fatty acids). This may be done very quickly by shaking up 1 to 2 grammes of sample with 10 c.c. of petrol-ether (·64); if insoluble soaps are present, a turbid or silky appearance is seen. The amount of insoluble soap sufficient to cause this silkiness, although small, has a decided influence on the pressing of such fatty acids; fatty acids containing insoluble soaps will not seed properly, and therefore will not press.

Alkalies and bases generally may be determined by adding excess of standard acid in presence of methyl orange, boiling well, filtering, and washing with boiling water until filtrate is free from acid, and titrating back.

The actual estimation of the insoluble soaps is best done by dissolving 5 grammes in 50 c.c. of ·64 petrol-ether, filtering through a weighed filter, and washing filter with petrol until fat free; distil off the petrol, and dry and weigh the filter. Commercial fatty acids may contain as much as 9 to 10 per cent. of insoluble soaps. The greatest offenders are the explosive manufacturers, who split fats for the glycerine only; the fatty acids are to them a bye-product. Water should always be examined for.

The following figures will show how far many commercial products are from reaching the normal 90 per cent. decomposition :—

Fatty Acids from	Specific Gravity.	Free Fatty Acids.	Unsaponifiable.	Iodine Value.	Non-Fats.	Cold Test.
Arachis	·9142– ·9150	40·19– 62·74	1·45– 2·33	...	...	52–69
Animal Oil	·9290	58·87	1·13	63–6	...	65
Bone Fat	·9193– ·9198	86·36– 88·13	6·99– 8·37	...	...	93–98
Firsts Castor	·9494	81·1	0·57	89·1	...	28
Seconds Castor	·9478	89·1	0·81	80	...	24
Cotton Oil	·9210– ·9242	74·4– 96·6	0·7– 1·29	111·3	Up to 2%	86–98
Herring, Malabar	·9316– ·9384	89·89– 93·4	0·79– 0·87	...	...	85–89
Japan Fish Oil	·9151– ·9245	89·5– 90·2	0·68– 0·91	78·4	...	60–71
Linseed Oil	·9164	78·6– 85·3	1·1– 1·18	167·7	...	27–43
Maize Oil	·9095– ·9109	88–91	1·9– 2·41	120–127	...	63–73
Rape Oil	·9053– ·9115	77·2– 88·9	1·22– 2·48	148·9	.	22–31
Salmon Oil	·9142	86·4– 87·7	0·93	...	...	66
Sea Elephant Oil	·9048	88–91	0·36	...	...	53
Seal Oil	·9112	90·24	0·99	...	...	59
Sesame Oil	...	99·41	...	...	...	78
Soya Bean Oil	·9059– ·9202	84·3– 91·7	0·97– 2·44	124–141	...	42–71
Tallow	...	90·1	...	...	...	107
Whale Oil	·9095– ·9255	72·62– 100	0·61– 1·59	107– 135·5	Up to 10%	70– 78° F.

FATTY ACID DISTILLATION.

The distillates obtained from autoclave fatty acids vary in test according to the raw material and the length to which the distillation has been carried.

Non-fatty matter is never present in distillates; if a sample offered as distillate contains non-fatty matter, it is a proof of incorrect description on the part of the party offering the sample. The molecular weight of the fatty acids in fatty acid distillates is almost invariably lower than 282, so that titration on 282 may give results 3 to 5 per cent. above the truth; the only safe method is to determine the unsaponifiable matter by extraction with petrol.

Fatty Acid Distillates.—

Specific Gravity up to ·9300.
Free Fatty Acids up to 98·5 per cent. gravimetric.
Unsaponifiable usually below 5 per cent.; may rise to 10 per cent. in bad samples.
Iodine Value 57 to 75.
Cold Test 20 to 120° F., according to origin.

It should not be forgotten that the iodine value of the distillates bears no relation to the iodine value of the original oil or fat. For example: An oil having an iodine value of 135 when autoclaved, decomposed, and the fatty acids distilled, gave a distillate having an iodine value of 75. The back ends of the distillate are usually redistilled, but the back ends from the more fluid oils have been sold as cloth oils.

Back Ends from Fatty Acid Distillation.—

Specific Gravity	·9128 to ·9760	Unsaponifiable	8·46 to 39·56%
Free Fatty Acids	31·02 to 87·77%	Cold Test	35 to 74° F.

The amount of combined fatty acids will of course depend upon the amount of undecomposed fat left in the fatty acids distilled.

The products from the gas condensers have also been marketed at times as textile oleines; these oils from the gas condensers are characterised by a more or less strong smell of acroleine.

OIL FROM GAS CONDENSERS.

Specific Gravity	·9067	Unsaponifiable	29·65%
Free Fatty Acids	66 to 100% as oleic	Cold Test	48 to 78° F.

Pressing of Fatty Acids.—The cold test of the oleine from the pressing of fatty acids is only dependent on the temperature at which the fatty acids are pressed.

The melting point of the stearine from the same fatty acids depends not only on the temperature at which the fatty acids are pressed, but also on the physical condition of the fatty acids themselves.

	FATTY ACIDS.	OLEINE.	STEARINE.
Free Fatty Acids	87·42	84·95	95·18
Cold Test	82° F.	24° F.	113° F.
Free Fatty Acids	91·65	88·13	100
Cold Test	74° F.	20° F.	113° F.

Candle Stearines.—The free fatty acids in distilled candle stearines when calculated to oleic acid are almost always over 100 per cent.; this is owing to the fact that the molecular weight of their fatty acids is usually from 265 to 275. These stearines are never entirely free from unsaponifiable matter, which may amount to from 2 to 3 per cent. in the poorer qualities. In saponified candle stearines the free fatty acids calculated as oleic acid may be as low as 93 per cent., even when the melting point is over 130° F. The iodine value varies with the source of the material, and also with the process used in manufacture, and may rise to 28. The ash should always be determined; an amount of ash that is immaterial for most purposes is fatal in a candle stearine; the percentage of ash should be so low as to be unweighable when 4 to 5 grammes of the sample are burned off. The melting point of the cold-pressed stearine varies with that of the distillate pressed, and also to some extent with the season of the year.

MELTING POINT OF DISTILLATE.	MELTING POINT OF COLD-PRESSED STEARINE.
88° F.	111° F.
90 ,,	110 ,,
90 ,,	112 ,,
72 ,,	115 ,,
75 ,,	117 ,,

This stearine is afterwards hot pressed in order to remove the last portion of the oil, the melting point of the hot-pressed stearine varying with the temperature at which the hot pressing is carried on, the time in the press, and also with the pressure applied.

MELTING POINT OF COLD-PRESSED STEARINE.	MELTING POINT OF HOT-PRESSED STEARINE.
111° F.	120° F.
112 ,,	126 ,,
117 ,,	128 ,,
118 ,,	133 ,,

The hot-press oil obtained during hot pressing is either redistilled or sold for textile soap making.

These hot-press oils usually test 95 to 100 per cent. free fatty acids, the unsaponifiable may rise as high as 7 per cent. The melting point varies with that of the cold-pressed stearine put through the hot presses.

The iodine value of the hot-press oil is governed more by the origin of the material than by the temperature at which the hot pressing takes place.

HOT-PRESS OILS.

Specific Gravity . . .	·9172 to ·9315	Open Flash	330 to 340° F.
Free Fatty Acids . .	95 to 100%	Melting Point	98 to 112 ,,
Unsaponifiable . . .	1·40 to 6·72%	Cold Test	87 to 109 ,,
Iodine Value . . .	71·2		

OLEINES FROM PRESSING OF FATTY ACIDS AND FATTY ACID DISTILLATES.

These oleines are of two classes:—

1. Saponification oleines, from the pressing of fatty acids, from decomposing after autoclaving or other splitting process.

2. Distillation oleines, from products which have been distilled after splitting and the distillate pressed.

Ten years ago the iodine values of saponification oleines ran from 65 to 80 per cent. lower figures than any distilled oleines on the market; this constitutes a good distinction between the two classes, but at the present time there are saponified oleines on the market with iodine values up to 140. The old distinction is now reversed, and at the present time an oleine with an iodine value over 110 is most probably a saponification oleine.

On distillation the undecomposed fat present in the material distilled is broken up, whilst in saponified oleines all the undecomposed fat is found in the oleine, and this difference in the amount of combined fatty acids present is the most definite difference between the two classes, and may in the case of saponified oleines rise to 18 per cent.

Distilled Oleines.		Saponification Oleines.
Per cent. Combined Fatty Acids.		Per cent. Combined Fatty Acids.
American Brown	1·11	From 5 to 18
Dutch ,,	3·41	
American ,,	0·66	
French ,,	0·61	
V ,,	0·98	

IODINE VALUES.

Distillation Oleines.		Saponification Oleines.	
American Pale	82·1 to 113·3	Belgian Pale	69·5
,, Brown	76·8 to 110	,, Brown	66·4
Australian Pale	77·9	English Pale	99·5
Belgian Pale	82·7	,, Brown	73·5 to 140
,, Brown	83·4 to 87·7	French ,,	82·5 to 132
Dutch Pale	82·2	Spanish Brown	80
,, Brown	80·5 to 86·1		
French Pale	84·4		
,, Brown	79·1 to 88·9		

Saponification Values.

American Brown	194 to 200	Dutch Pale	195
Australian Pale	204	English Brown	180 to 195
,, Brown	208		

REFRACTIVE INDICES AT 70° F.

American Pale, Distilled	1·4666 to 1·4676	Dutch Pale, Distilled .	1·4616 to 1·4621
,, Brown, ,,	1·4596 to 1·4676	,, Brown, ,, .	1·4636
Australian Pale, ,,	1·4626	English Pale, ,, .	1·4656 to 1·4700
Belgian Pale, ,,	1·4626 to 1·4656	,, Brown, ,, .	1·4645
,, Brown, ,,	1·4626 to 1·4676	French Pale, ,, .	1·4646
,, ,, Saponified	1·4626	,, Brown, ,, .	1·4636

Unsaponifiable.—In saponified oleines the unsaponifiable should never rise above 2·5 per cent., but in distilled oleines the amount of unsaponifiable will depend on the raw material, the care taken during distillation, and also on the amount of distillate collected for pressing.

At the present time oleines are usually sold on the percentage of saponifiable matter they contain, so the only thing necessary is to see that the test of the bulk is equal to that of the sample which was bought on.

The molecular weight of the fatty acids from oleines do not vary far from that of oleic acid (282), from 270 to 287.

Evaporation Loss on Heating to 212° F. for Three Hours.	
Belgian Brown, Distilled . . .	0·43 per cent.
English ,, ,, . . .	0·52 ,,
American ,, ,, . . .	0·67 ,,

VISCOSITY AT 70° F., REDWOOD.		IODINE VALUES.
American Pale, Distilled . . .	198	87
,, Brown, ,, . . .	180	89
Australian Pale, ,, . . .	152	80
Dutch Pale, ,, . . .	168	82
,, Brown, ,, . . .	206	85
English Brown, ,, . . .	205	86
,, Saponified . .	212	...
French Brown, Distilled . . .	185	84

The above figures show that contrary to what one would expect from analogy to the fatty oils, there is not even a general relation between iodine value and viscosity.

Oxidised Fatty Acids.—Here again the percentage of oxidised acids, though only small, has a most decided influence on the colour of the oleine:—French Brown distilled, 0·85 per cent.; American Brown distilled, 1·35 per cent.

It will be found that, taking different samples of the same make, the lower the cold test, the higher the unsaponifiable and iodine values will be.

"Gilding."—Liability of oleines to cause staining of woollen goods, technically called gilding.

The cause is the presence of fatty acids from semi-drying and drying oils in the oleine. The liability of an oleine to cause gilding is much increased in the presence of water. An oleine that will not stain pieces or yarn, even after lying in pile in the grease for a year, will do so in two or three months if water has any access to the goods—say, through a defective roof. When the goods come to be scoured, bleached, and finished these stains show up more plainly than ever. Up to the present no method of removing these stains on a commercial scale has been found, the latest process put forward being the use of hydrosulphite of soda (Hyraldite, Rongalite, etc.) and soap. This certainly removes part of the stain, but the stain is still quite visible even after repeating this treatment three times.

At the present time there are so many mixtures sold as oleine that the iodine value, in spite of the reliance placed upon it by most people, is of no value whatever. The figures from Ballantyne's Specific Temperature reaction are much more reliable, and are obtainable in a few minutes. Mackey's oil tester also gives reliable results within three hours.

A mixed oleine used for white yarn, and known to cause gilding, even when the yarn was kept quite dry, had an iodine value of 62·3—a figure which would be considered as beyond question by anyone who judged by iodine value only—but the same sample in Mackey's tester rose to 240° F. in one hour, and to 300° F. in eighty-two minutes. The specific temperature reaction of the same sample was 106. These are figures to be expected from an oleine which is known to cause gilding of dry yarn. It may be taken that there is no certainty that an oleine will not cause gilding if it rises above a temperature of 215° F. in two hours in Mackey's tester, or if it has a specific temperature reaction higher than 90. If the specific temperature is not over 100, it will only gild under exceptional circumstances.

In these oleines, like those from recovered products, the refractive index rises with the fall of the cold test.

A sample of French brown oleine, after keeping for twelve months, had separated a large amount of stearine (over 90 per cent.), the liquid portion was poured off, and the liquid and solid portions tested separately.

	Liquid Portion.	Solid Portion.
Refractive Index	1·4680	1·4666
Cold Test	42° F.	54° F.

For the B.P. tests for Acidum oleicum, see the B.P. limits at the end of the book.

Oleine.	Specific Gravity.	Iodine Value.	Refractive Index at 70° F.	Saponifiable Value.	Free Fatty Acids as Oleic.	Combined Fatty Acids.	Unsaponifiable.	Viscosity at 70° F.	Open Flash.	Cold Test.
Australian White .	·8936–·8973	77·9	1·4676	...	95·18–100	...	2·31–4·36	168	330–356	36–48
Australian White .	·8943–·8968	79·6	1·4626	...	98·7–100	...	2·32–2·70	...	342–360	37–44
Australian Brown .	·9078	...	1·4616–1·4676	...	96	...	2·44	...	...	70
American White . .	·8960–·9042	87·1	1·4632–1·4666	...	96·23–99·41	...	3·2–3·9	198	328–340	24–41
American White . .	·8963	82·1	...	...	96·94	...	3·56	...	...	43
American Brown . .	·9004–·9040	98·7	1·4676	194	93·41–99·41	...	2·7–7·22	...	338–350	30–47
American Brown . .	·8969–·9006	85–89·1	1·4596–1·4651	...	97·29–100	0·66	3·24–3·95	180	330–345	30–47
American Brown . .	·8973–·9011	100·6	1·4656	200	95·5–99·4	1·11	2·94–5·7	...	330–350	22–29
American Brown . .	·8993–·9050	104·7	1·4636	...	93·2–98·7	...	3·99–7·17	..	330–348	22–40
American Brown . .	·8950–·9047	80·5	1·4626	...	96·5–100	...	1·75–4·92	...	332–353	30–49
Belgian White . .	·9025–·9120	69·5–82·7	...	...	98·7–100	...	1·29–4·88	...	...	56–60
Belgian Brown . .	·9000–·9170	66·4–87·7	...	...	84·9–96·2	...	1·35–6·19	..	...	42–61
Cocoanut Oleine . .	·9110	...	...	...	86·36	...	3·25	...	...	58
Cotton Oleine filtered .	·9040–·9050	99·5	1·4705	...	95–97	...	3·6–6·0	...	343–346	39–44
Cotton Oleine unfiltered	·9010–·9239	83·4	1·4715	...	95–97	...	3·7–5·9	...	340–348	54–76
Dutch White . .	·8991–·9084	84·4	1·4650	...	94·1–95·5	...	5·72–7·72	...	336–350	41–51
Dutch White . .	·8940–·8982	82·2	1·4621	196	95·9–100	...	2·68–4·20	168	335–352	35–43
Dutch White . .	...	...	1·4616	...	98·7	...	3·86	...	...	47
Dutch Brown . .	·9000–·9021	80·5–85·4	1·4687	...	89·9–96·6	3·41	4·22–7·85	...	336–360	37–44
Dutch Brown . .	·8974–·9000	82·3	1·4636	...	94·5–96·6	...	4·66–6·94	206	350–368	35–46
Dutch Brown . .	...	86·1	1·4636	...	97·3	...	5·55	...	334	40
English Brown . .	·8971–·9083	84·4	1·4645	196	88·1–100	...	3·22–7·16	205	334–354	46–59
French White . .	·9000	...	...	...	95·8–100	...	1·7–3·9	...	...	36–49
French Brown . .	·8990–·9035	82·4	1·4660	...	90·2–92·7	0·98	5·25–7·5	...	334–350	41–54
French Brown . .	·8987–·9063	79–88·9	1·4636	...	95·4–100	0·61	1·74–6·5	185	333–350	26–51

SECTION VIII.

GLYCERINE.

Qualitative Detection.—Heat the substance to be tested in a test-tube with twice its weight of potassium bisulphate; if glycerine is present, acroleine is given off, possessing a most penetrating odour, and causing a copious flow of tears. Commercial glycerines are derived from two sources:—

1. The waste lyes of the soap-maker.
2. The splitting of fats by open processes or in the autoclave, by the candle-maker or explosive-maker.

The second class is always the purest, and the easiest to work up for dynamite glycerine or for "chemically pure."

The soap-makers' crude of the present time is a very different article to that of twenty years ago. A first-class soap-maker's crude at the present time does not contain 10 per cent. ash, whilst candle-makers' crude is usually sold on a basis of 0·5 per cent. ash, with an allowance for every 0·1 per cent. above or below this figure.

All commercial glycerine is bought and sold on the results obtained by the official method, which is given below.

The following method of the International Committee of 1911 must be used for all analyses in buying and selling:—

Sampling.—The most satisfactory method for sampling crude glycerine liable to contain suspended matter, or which is liable to deposit salt on setting, is to have the glycerine sampled by a mutually approved sampler as soon as possible after it has been filled into drums, but in any case before separation has taken place. In such cases he shall sample with a sectional sampler, then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerine. Each drum must be sampled.

Glycerine which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerine to be taken, including any deposit.

Analysis.—1. *Free caustic alkali.*

Weigh 20 grammes of sample into a 100 c.c. flask, dilute with about 50 c.c. of freshly boiled distilled water, and add an excess of neutral barium chloride solution, 1 c.c. phenolphthalein, make up to the mark with freshly boiled distilled water, and mix. Allow the precipitate to settle, draw off 50 c.c. clear liquor, and titrate with N/1 acid, calculate to Na_2O present as caustic alkali.

2. **Ash and Total Alkalinity.**—Weigh 2 to 5 grammes into a platinum

dish, burn off the glycerine over a luminous Argand burner, the temperature being kept low to avoid volatilisation and formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot water, filter, wash, filter, ignite the residue in the platinum dish, return filtrate and washings to the dish, evaporate, and carefully ignite without fusion, and weigh the ash. Dissolve the ash in distilled water, and titrate the total alkalinity, using methyl orange cold or litmus boiling.

3. **Alkali present as Carbonate.**—Weigh 10 grammes, dilute with 50 c.c. of distilled water, and add sufficient N/1 HCl to neutralise the total alkali found at (2), boil under reflux condenser for ten to twenty minutes, wash down the condenser tube with distilled water free from carbon dioxide, and titrate back with N/1 NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O, then deduct the Na_2O found in (1). The difference equals the Na_2O existing as carbonate.

4. **Alkali combined with Organic Acids.**—The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O combined with organic acids.

5. **Determination of Acidity.**—Weigh 10 grammes, dilute with 50 c.c. of carbon dioxide-free distilled water, and titrate with N/1 alkali and phenolphthalein; express in term of Na_2O required to neutralise 100 grammes.

6. **Total Residue at 160° C.**—For this the crude should be slightly alkaline with Na_2CO_3, not exceeding the equivalent of 0·2 per cent. Na_2O in order to prevent the loss of organic acids. To avoid the formation of polyglycerols, this alkalinity must not be exceeded.

Preparation of Glycerine.—Ten grammes are weighed into a 100 c.c. flask, diluted with water, and the calculated quantity of N/1 HCl or N/1 Na_2CO_3 added to give the required degree of alkalinity. The flask is made up to the mark, mixed, and 10 c.c. measured into a weighed Petri or similar dish of 2½″ diameter and 1½″ deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 milligrammes.

Evaporation of the Glycerine.—The dish is placed on a water bath (the top of the 160° C. oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 11 cubic inches having an iron plate, ¾ inch thick, lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerine is placed. If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130 to 140° C. can be maintained with the door partly open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool. An addition of 0·5 to 1·0 c.c. of distilled water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the 160° C. oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important, but is usually two to three hours. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven—

the temperature of which is carefully maintained at 160° C.—for one hour, when it is removed, cooled, and the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid, and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1·5 milligramme per hour is obtained.

Corrections to be Applied to the Weight of the Total Residue.—In the case of acid glycerines a correction is to be made for the alkali added : 1 c.c. N/1 alkali represents an addition of 0·022 gramme. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the sodium hydrate and carbonate to sodium chloride. The corrected weight multiplied by 100 gives the percentage of total residue at 160° C. Preserve the total residue for the determination of the non-volatile acetylisable impurities.

7. **Organic Residue.**—Subtract the ash from the total residue at 160° C. Repeat as organic residue at 160° C. (*N.B.*—The alkaline salts of organic acids are converted into carbonates on ignition, and that the carbon dioxide radicle thus derived is not included in the organic residue).

8. **Moisture.**—This estimation is based on the fact that glycerine can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphorus pentoxide.

Two to 3 grammes of very pure bulky asbestos, freed from acid soluble material, and which has been previously dried in a water oven, is placed in a small stoppered weighing bottle of about 15 c.c. capacity. The weighing bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid under a pressure equivalent to 1 to 2 mm. mercury until constant in weight. From 1 to 1·5 gramme of glycerine is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is then taken and the bottle replaced in the desiccator under 1 to 2 mm. mercury pressure until constant in weight at 15° C.; this takes about forty-eight hours; at lower temperature the test is prolonged. The acid in the desiccator must be frequently renewed.

ACETIN PROCESS FOR GLYCEROL DETERMINATION.

This process is the one agreed upon at a conference of delegates from the American, British, French, and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on "crudes" in general, and is to be the process used (if applicable) whenever only one method is employed. On pure glycerine the results are identical with those of the dichromate process. For the application of this process the crude should not contain over 50 per cent. of water.

Reagents Required.

A. Best acetic anhydride. This should be carefully selected. A good sample must not require more than 0·1 c.c. N/1 NaOH for saponification of the impurities when a blank is run on 7·5 c.c. Only a slight colour should develop during digestion of the blank.

B. Pure fused sodium acetate. The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

C. A solution of caustic soda, for neutralising, of about N/1 strength, free from carbonate.

This can be readily made by dissolving pure NaOH in its own weight of water (preferably free from carbon dioxide), and allowing to settle until clear, or filtered through an asbestos or paper filter. The clear solution is diluted with carbon dioxide-free water to the strength required.

D. N/1 NaOH, free from carbonate, prepared as above, and carefully standardised.

E. N/1 acid, carefully standardised.

F. Phenolphthalein solution, 0·5 per cent. in neutralised alcohol.

Procedure.—Into a narrow-mouthed flask (preferably round bottomed), capacity about 120 c.c., and which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25 to 1·5 gramme of glycerine. Add first about 3 grammes of the anhydrous sodium acetate, then 7·5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. wide inside. The flask is connected to the condenser either by a ground glass joint (preferably) or by a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour. Heat the contents of the flask and keep boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask. Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of the carbon dioxide-free water heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapour from the flask on adding the water, and to avoid breaking the flask.

Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until solution is complete, except for a few dark flecks representing organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of condenser tube, detach the flask, wash off stopper or ground glass connection into the flask, and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity. Wash filter thoroughly with cold distilled water free from carbon dioxide until the washings are acid free, add 2 c.c. of phenolphthalein solution, then run in caustic soda solution C or D until a faint pinkish yellow colour appears throughout the solution. This neutralisation must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free distilled water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

From a burette 50 c.c. or a calculated excess of N/1 NaOH (D) is now run in and the exact amount noted carefully. It is boiled gently for fifteen minutes, the flask being fitted with a glass tube as partial condenser, cooled as quickly as possible, and the excess of NaOH titrated with N/1 acid (E) until the pinkish yellow or chosen end point just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end point taken.

From the N/1 NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below: 1 c.c. NaOH N/1 equals 0·03069 gramme glycerol.

The coefficient of expansion for normal solutions is approximately 0·00033 per cubic centimetre for each degree centigrade. A correction should be made on this account, if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analyses.

After neutralising the acetic acid it is not necessary to add more than 5 c.c. of the N/1 alkali (D), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

Determination of the Acetylisable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 c.c. of distilled water washed into a clean acetylising flask of 120 c.c. capacity and the water evaporated. Now add acetic anhydride and anhydrous sodium acetate, and proceed as in the glycerol determination before described, and calculate the result to glycerol.

Analysis of Acetic Anhydride.—Into a weighed stoppered vessel containing 10 to 20 c.c. water run about 2 c.c. of the acetic anhydride, replace stopper, and weigh; allow to stand, with occasional shaking, for several hours, until all the acetic anhydride is hydrolised; then dilute to about 200 c.c., add phenolphthalein, and titrate with N/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of sample, stopper, mix, allow to cool, and weigh. Wash contents into about 20 c.c. of cold water, and titrate acidity as before. This yields the acidity due to the original preformed acetic acid plus half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 grammes) and double the result, obtaining cubic centimetres N/1 NaOH per 100 grammes of sample: 1 c.c. N/1 NaOH equals 0·0510 acetic anhydride.

DICHROMATE PROCESS FOR GLYCEROL DETERMINATION.

Reagents Required.

A. Pure potassium dichromate powdered and dried in air free from dust or vapours at 110 to 120° C. This is taken as the standard.

B. Dilute dichromate solution. 7·4564 grammes of the above dichromate (A) are dissolved in distilled water and the solution made up to 1 litre at 15·5° C.

C. Ferrous ammonium sulphate. Dissolve 3·7282 grammes dichromate (A) in 50 c.c. water, add 50 c.c. of 50 per cent. (by vol.) sulphuric acid, and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute dichromate (B); calculate the value of the ferrous sulphate in terms of dichromate.

D. Silver carbonate. This is prepared as required for each test from 140 c.c. of 0·5 per cent. silver sulphate solution by precipitation with about 4·9 c.c. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used; any excess of alkaline carbonate prevents rapid settling), settle, decant, and wash once by decantation.

E. Subacetate of lead. Boil pure 10 per cent. solution of lead acetate with an excess of litharge for one hour, keeping the volume constant, and filtrate while hot. Disregard any precipitate which subsequently forms, and preserve out of contact with carbon dioxide.

F. Potassium ferricyanide. A very dilute solution containing about 0·1 per cent.

Procedure.—Weigh 20 grammes of the glycerine, dilute to 150 c.c., and take 25 c.c.; add the silver carbonate, allow to stand, with occasional agitation, for about ten minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (E); allow to stand a few minutes, dilute with distilled water to 100 c.c., and then add 0·15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c. and returning the filtrate if not clear and bright; test a portion of the filtrate with basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 c.c. is ample). Occasionally a crude will be found requiring more, and in this case another aliquot of 25 c.c. dilute glycerine should be taken and purified with 6 c.c. basic acetate. Care must be taken to avoid marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium dichromate and sulphuric acid), add 3·7282 grammes dichromate (A), rinse down the dichromate with 25 c.c. water, and stand, with occasional shaking, until all the dichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50 per cent. (by vol.) sulphuric acid, and immerse the vessel in boiling water for two hours, and keep protected from dust and organic vapours, such as alcohol, till the titration is completed; add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F); titrate back with the dilute dichromate. From the amount of dichromate reduced calculate the percentage of glycerol: 1 gramme glycerol equals 7·4564 grammes dichromate, and 1 gramme dichromate equals 0·13411 gramme glycerol.

Notes.—1. It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

2. Before the dichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid, as stipulated in the process.

3. For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0·5 c.c.

4. It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

Instructions for Calculating the Actual Glycerol Content.—1. Determine the apparent percentage of glycerol in the sample by the acetin process, as described. The result will include acetylisable impurities if any be present.

2. Determine total residue at 160° C.

3. Determine the acetin value of the residue at (2) in terms of glycerol.

4. Deduct the result found at (3) from the percentage obtained at (1).

Report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

Notes and Recommendations.—Experience has shown that in crude glycerine of good commercial quality the sum of water, total residue at 160° C., and corrected acetin result come to within 0·5 per cent. of 100.

Further, in such crudes the dichromate result agrees with the uncorrected acetin result to within 1 per cent.

In the event of greater differences being found, impurities such as polyglycerols or tri-methylene glycol are present.

Tri-methylene glycol is more volatile than glycerol; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and dichromate results of such distillates. Tri-methylene glycol gives by the former method 80·69 per cent. and by the latter 138·3 per cent., expressed as glycerol. In valuing crude glycerine for certain purposes it is necessary to ascertain the approximate proportion of arsenic sulphide, sulphites, and thiosulphites. The methods for detecting and determining these impurities have not formed the subject of this investigation.

Recommendations by the Executive Committee.—If the non-volatile organic residue at 160° C. in the case of a soap lye crude be over 2·5 per cent.—*i.e.* when not corrected for CO_2 in the ash—then the residue shall be examined by the acetin method, and any excess of glycerol found over 0·5 per cent. shall be deducted from the acetin figure. In the case of saponification, distillation, and similar glycerines, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent. the organic residue must be acetylated, and any glycerol found (after making the deduction of 0·5 per cent.) shall be deducted from the percentage of glycerol found by the acetin method.

SAMPLING CRUDE GLYCERINE.

The usual method of sampling crude hitherto has been by means of a glass tube, which is slowly lowered into the drum, with the object of taking as nearly as possible a vertical section of the glycerine in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates viscous glycerines run into the tube very slowly, so, owing to the time occupied, it is impossible to take a complete section of the drum. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt in the drum. A sampler has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out of each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire depth of the drum. By this arrangement the glycerine fills into the sampler almost instantaneously. But there are also a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when a sampler is open or closed. In samplers of larger section than 1 inch it is possible to arrange a third motion whereby the bottom ports only are open for emptying, but in samplers of smaller dimensions this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom the ports are opened for a second or two, then closed and withdrawn; the sample is discharged into the receiving vessel by opening the ports. When the drum contains suspended salts the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum. It is therefore recommended that the drum should be sampled before the salt has settled.

A 1 inch sampler[1] withdraws about 10 oz. from a 10 cwt. drum.
A ½ ,, ,, ,, ,, 5 ,, ,, 10 ,, ,,

The quality of crude glycerine is dependent on the close watching of many small points. The following figures show that if the autoclaving has been carefully done there is no advantage in waiting any length of time before drawing off the sweet water:—

Sweet Water from Autoclave.	Percentage of Oil.
Immediately after separation	0·14
Settled for ½ hour	0·19
,, ,, 1 ,, ...	0·16
,, ,, 1½ hours	0·15
,, ,, 2 ,, ...	0·15
,, ,, 2½ ,, ...	0·19
,, ,, 3 ,, ...	0·19

Oil determined by shaking out 100 c.c. with ether meth. in separator:—

Acidity of Sweet Water.	Before Ether Extraction.	After Ether Extraction.
Unsettled	2·5 c.c. N/10 KOH	2·0 c.c
Settled for ½ hour	2·5 ,, ,,	2·0 ,,
,, ,, 1 ,, ...	2·4 ,, ,,	2·0 ,,
,, ,, 1½ hours	2·5 ,, ,,	2·0 ,,
,, ,, 2 ,, ...	2·5 ,, ,,	2·1 ,,
,, ,, 2½ ,, ...	2·4 ,, ,,	2·0 ,,
,, ,, 3 ,, ...	2·3 ,, ,,	2·0 ,,

The acidity was determined by titrating 100 c.c. with N/10 KOH and phenolphthalein.

If the autoclaving has been carelessly done there may be considerable difficulty in getting a separation, even to the point of having acid to add in order to obtain separation at all.

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[1] Authorised makers of sampler Messrs Young & Co., 47–49 Stanley Street, Kinning Park, Glasgow.

Sweet water settled three hours and evaporated down to 140° C. :—

Residue at 160° C. . . .	1·07 per cent.
Ash	0·14 per cent.
Acidity	0·98 per cent. as oleic acid.

Sweet water settled for three hours, and then extracted with ether, and evaporated down to 140° C. :—

Residue at 160° C. . . .	0·76 per cent.
Ash	0·15 per cent.
Acidity	0·70 per cent. as oleic acid.

Saponification Crude.—A bad sample which could not be filtered in its original state, even when hot, gave the following figures :—

Residue at 160° C. . . .	4·53 per cent.
Ash	3·40 per cent.

After treatment the ash in this sample fell to 1·74 per cent. A large amount of the residue in this sample was soaps of alkaline earths, caused by careless decomposing.

Crude glycerine is usually sold on a basis of so much per ton for a given percentage of glycerol, with rebate below and allowance above. A reduction of so much per ton is usually made if the ash in the sample rises above a given figure. The crude must have a given specific gravity, usually 1·26. The acidity in some samples of saponification crude rises above 3 per cent., expressed as oleic acid ; this of course adds to the difficulty of purification.

Crude glycerine, both saponification and soap lye, always separate fatty matter on concentration. This separated grease is a curious product, and has practically no value. The worst sample of this grease the writer has seen sank in water, and after washing (by kneading in water) and drying gave the following figures :—

Non-fatty Matter . . .	49·62 per cent.
Fatty Acids	50·38 per cent.

The fatty acids contained oxidised acids, with molecular weight 328, to the extent of 16·8 per cent. on the dried sample, which leaves only 33·58 per cent of the dried grease available for the soap-maker or distiller.

SECTION IX.

RESINS.

QUALITATIVE DETECTION.

Liebermann-Storch Reaction.—Dissolve a small amount of the fat, or better the fatty acids, in a few cubic centimetres of acetic anhydride, warming if necessary; cool, and drop in sulphuric acid (34·7 c.c. of concentrated sulphuric acid and 37·5 c.c. of water). The presence of resin is shown by an evanescent violet colouration when only small amounts are present; if large quantities are present, the colouration persists for some time.

Commercial resins from all sources consist practically of nothing but free fatty acids and unsaponifiable matter. This is shown by the fact of the amount of unsaponifiable matter that can be extracted from the sample being the same whether the sample has been dissolved up in alcohol, the free fatty acids titrated with aqueous alkali, and the unsaponifiable matter extracted with petrol-ether, or whether it has been saponified by boiling with alcoholic potash, and the unsaponifiable matter extracted in the usual way.

Sample.	Free Fatty Acids as Oleic.	Unsaponifiable.	Molecular Weight.
	Per cent.	Per cent.	
American B. . . .	76·85	9·03	
,, E. . . .	78·61 to 84·95	4·95 to 5·66	320
,, F. . . .	76·85 to 88·13		
,, G. . . .	85·31 to 88·13		
,, H. . . .	80·02 to 87·77	2·28 to 5·62	331
Burgundy Pitch . .	66·98	3·49	
French A.A. . . .	83·19	5·57	
,, D. . . .	83·54 to 86·01	5·65	
,, F. . . .	90·59		
,, G. . . .	91·65		
,, H. . . .	81·08 to 82·40	4·77 to 4·89	336 to 360
,, J. . . .	84·25	4·57	
,, K. . . .	86·36	3·73	
,, W.W. . .	85·31	4·08	
,, W.G. . .	84·95	5·49	
Greek F. . . .	77·2 to 86·41	3·45	319
Mexican . . .	77·54 to 82·84	7·05 to 8·84	
Portuguese . . .	84·25	7·67	314
Spanish X. . . .	84 60		
,, No. 2 . .	82·13	4·27	
,, No. 8 . .	82·13	4·56	
Venice Turpentine . .	88·0		

It is exceedingly difficult to obtain any approach to accuracy when working on resins. Experiments were made with great care on a sample of American H. resin. 2·57 grammes were taken, and the saponifiable and unsaponifiable estimated. The following figures were obtained :—

Unsaponifiable,	0·1170 gramme,	equal to 4·55 per cent.
Saponifiable,	2·4430 grammes,	,, ,, ,,
Total,	2·56 grammes, loss 0·01 gramme.	

The fatty acids (molecular weight 331) were dissolved in 50 c.c. of petrol-ether to separate the petrol insoluble acids.

2·443 grammes were taken, giving the following figures :—

Petrol, soluble,	2·079 grammes.	
,, insoluble,	0·4370 gramme,	equal to 14·90 per cent.
,, total,	2·5160 grammes.	

This is a gain of 0·730 gramme, equal to practically 3 per cent.

An experiment was made to determine the loss, if any, on heating resin in the water oven. A sample of American H. resin gave a loss of only 0·26 per cent. after six days' heating.

A sample of Greek resin with free fatty acids 85·16 per cent., unsaponifiable 0·95 per cent., molecular weight of fatty acids 319, gave petrol soluble acids 95 per cent., molecular weight of fatty acids 340, petrol insoluble acids 4·14 per cent., molecular weight of fatty acids 235.

The molecular weight of the acids insoluble in petrol was such a startling figure that it was repeated, but again gave the same result. This result raises a grave doubt as to these petrol insoluble acids being oxidised acids at all. Every other sample of petrol insoluble acids, with the exception of those from resin, have a molecular weight decidedly higher than the molecular weight of the petrol soluble acids from the same sample. In this case also, like the American H. resin, the total weights came to more than the weight taken. The petrol insoluble acids from the Greek sample took two days in the oven to come to a constant weight.

Resin in Mixtures.—A general process for the estimation of resin in mixtures has yet to be worked out. In mixtures with neutral oils, mineral oils, vaselines, and mineral waxes, simple titration on a molecular weight of 330 is usually as near the truth as any other method. In cases where any quantity of free fatty acids are present, titration is of course no good. In such cases the Twitchell process is the only one available. The greatest drawback to this process is the fact that oxidised acids (from which no samples are entirely free) are not converted into ethyl ethers during the process. The removal of the oxidised acids removes anything up to 25 per cent of the resin present, so that no quantitative results can be obtained by treating the petrol soluble portion by Twitchell's process.

It will be found that results as good can be obtained by determination of the refractive index, and calculation from the refractive index of good samples of the article under examination, or of the iodine values. A scale of colour has been fixed for the different grades of American resin, and made official for the United States.

The table gives the amount of yellow and red on Lovibond's scale, to which the different grades must conform :—

	YELLOW.	RED.		YELLOW.	RED.
W.W. . .	20	2·1	I. . . .	40	7·6
W.G. . .	20	2·5	H. . . .	45	9·4
N. . . .	25	3·3	G. . . .	50	15·5
M. . . .	30	4·5	F. . . .	75	34·5
K. . . .	35	5·8	E. . . .	100	52·5

QUANTITATIVE ESTIMATION.

Twitchell's Process.—The amount of sample to be weighed out is governed by the fact that after saponifying and removing the unsaponifiable, decomposing the soap with acid, and shaking out with ether, the weight of the remaining fatty acids is found to be about 5 grammes.

Etherification.—The fatty acids are weighed into a 300 c.c. flask, dissolved in 50 c.c. of absolute alcohol, and etherified by leading in a steady stream of hydrochloric acid gas until the solution is saturated (this requires from one to two hours), the flask containing the alcoholic solution to be cooled in water, keeping the temperature as low as possible. The resin fatty acids present do not form ethyl ethers. After the hydrochloric acid treatment the flask is allowed to stand for half an hour at room temperature, water is added to five times the volume of the flask contents, and the whole boiled under reflux for fifteen minutes. After cooling, the liquor is poured into a separator, and shaken out, first with 100 c.c. and then with 50 c.c. of ether, repeating if necessary until the ether remains colourless. Neutralise the aqueous solution with alkali, and evaporate down to about 50 c.c., cool, and pour back into the separator, acidify, and again shake out with ether, using 25 c.c. each time, until the ether remains colourless. All the ether extracts are united in a separator and shaken out with 50 c.c. alkali (10 grammes of caustic potash, 10 grammes of alcohol, and 100 c.c. of water), any brown middle layer to be run off with the alkaline solution. The ether solution is then washed with water until the water remains colourless, then shake out again with 10 c.c. of the alkali solution, which is followed by water as before. The united alkali and water washings are again shaken out with 50 c.c. of ether to remove any remaining traces of ethyl ethers, and this ether washed with 10 c.c. alkali, followed by water, and these are united to the other alkali and washings. The alkaline solution is now acidified and shaken out with ether (50 c.c. each time) until the ether remains colourless.

The acid liquor is neutralised, evaporated down to 50 c.c., again acidified, and shaken out with ether. The united ether extracts are washed with water, the ether distilled off, and the residue dried and weighed as resin acids. The German customs again treat the fatty acids obtained by Gladdong's process, but the errors in the whole process are so considerable, that there does not seem to be much gain for the extra time spent, especially as the main errors lie in the Twitchell half of the process.

SECTION X.

RECOVERED PRODUCTS.

LIQUID RESIN.

This is a bye-product of the sulphite process for preparing wood pulp for the paper-maker. It has been offered also under the German name of tall oil. There are oils on the market of two distinct classes; both are dark brown treacly fluids, but the two classes can be distinguished by their different smell. The one class—and this was the first to be marketed—has a very strong empyreumatic smell, and the second class carries a pronounced acetous smell; this class is quite useless for distillation, at any rate in the state in which it is at present marketed.

In addition to the smell, these samples may be distinguished from each other by placing about a gramme of the sample in the water oven, when the normal samples are quite liquid after heating at this temperature for one hour, but the acetous samples are quite solid, having dried like a varnish.

Normal samples gave the following figures:—

Specific Gravity	·9506 to 1·0111	Open Flash	346 to 360° F.
Free Fatty Acids	70·50 to 87·77%	Water	Up to 11%
Unsaponifiable	6·75 to 10·80%	Cold Test	24 to 64° F.
Iodine Value	145·7		

A fuller examination of the saponifiable matter from liquid resin gave

Fatty Acids insol. in Ether	0·63 per cent.
,, ,, Petrol	9·6 per cent., with molecular weight 426.

The molecular weight of the normal fatty acids of the same sample was 330, a figure not far from that of ordinary resin.

A curious feature of these liquid resins is, that although the original sample may have a cold test of 30° F. or lower, the unsaponifiable matter and also the fatty acids of the sample are both quite solid at laboratory temperatures:—

Specific Gravity	1·2959
Free Fatty Acids	14·45 per cent.
Unsaponifiable	0·15 ,,

The second class did not appear on our markets until about two and a half years after the first, and is distinguished from the first by the much higher percentage of oxidised acids it contains, which may be as high as 40 per cent. This is the only case up to now in which a high percentage of oxidised acids is found together with a low percentage of free fatty acids.

Distillates from Liquid Resins.—The colour of these varies from amber to brown, and they all turn darker on exposure to air and light. The smell is slightly empyreumatic, but very much less strong than that of the original oil. These distillates have been placed on the market as oleines :—

Specific Gravity	·9443 to ·9633	Iodine Value	94·8
Free Fatty Acids	69·44 to 83·84%	Open Flash	344 to 352° F.
Unsaponifiable	12·20 to 26·06%	Cold Test	36 to 53° F.

RECOVERED GREASES.

Many processes have been proposed and patented for the recovery of greases and black oils from the soapy liquors of the textile manufacturer, but decomposition with acids, which was one of the earliest methods, is, in this country at any rate, used in the production of the major portion of the grease marketed; the only alternative that is used to any extent is the extraction with solvents, usually petrol or carbon disulphide.

On decomposing the soapy liquors with acid a layer of mixed grease, dirt, and fibre settles to the bottom of the tank, the acid liquor is run off, the magma allowed to drain, and then packed into bags, and again allowed to drain further. The bags are then put into a closed press fitted with an open steam-pipe. The press is closed up, and steam turned on and allowed to heat the press and contents for about an hour. Pressure is then applied, and a mixture of grease and water runs from the press into a well, the water being pumped away, and the grease pumped into a tank and heated with closed steam in order to separate the water from the grease; after separation the water is run off, and the grease packed into barrels.

For works purposes the commercial process is carried out on a definite volume in the laboratory.

The magma from fulling only gives	Black Oil or Soft Grease.
,, ,, ,, and warp washing gives	Black Oil or Medium Grease.
,, ,, wool ,, ,,	Medium and Hard Grease.
,, ,, ,, washing only ,,	Hard Grease.

Other materials pressed hot in the same way are Shoddy Dust, giving Black Oil; Engine Cloths and Waste, giving the so-called "Pressed Black Oils," which are of very low quality; Magma from Sewage Works, yielding Black Oils, Soft Grease, Medium Grease, and Hard Grease; and Magma from Calico Printing Works, giving Printers' Grease.

Examination of Magma.—Magmas should always be first examined in order to be certain that all the soap has been decomposed before proceeding with the examination.

Water.—Ten grammes are weighed into a beaker containing a glass rod, and the sample dried in the water oven until it is free from water drops.

Fat.—The residue from the water estimation is extracted with ether, and the ether filtered into a weighed flask; this is often a tedious operation, as the dirt is very finely divided and stops up the pores of the filter paper. The Soxhlet patent gives no advantage for the same reason. The ether is then distilled off, and the residual fat dried in the oven and weighed. The dirt is taken as the difference between fat water and 100.

Average Figures.—

Water	20·70 to 77·84 per cent.
Fat	3·72 to 67·55 ,,
Dirt	1·50 to 39·09 ,,

In order to find whether the magma from a given source will give a good or poor yield of grease on pressing, when calculating out the results the percentage of grease must be calculated on the dry magma after driving off the water.

The cake left in the press is called sud cake. The amount of grease left in the sud cake varies with the care taken with the pressing, and in bad cases may be as high as 35 per cent. The sud cake is sometimes extracted with solvents to recover the residual grease. The grease recovered in this way is always to be classed amongst the hard greases.

GREASES EXTRACTED FROM SUD CAKE.

Specific Gravity	·9539 to ·9685	Water	0·81 to 3·21
Free Fatty Acids	17·63 to 19·39%	Dirt	2·26 to 31%
Unsaponifiable	32·31 to 36·02%	Cold Test	86 to 91° F.

The cake left after solvent extraction gave—

Grease, 4·26 per cent.; Water, 2·60 per cent.; Dirt, 93·14 per cent.

The sud cake is usually ground up and sold for manure, but owing to the low percentage of nitrogen contained, it has not much value. The sud cake from mills where indigo dyeing is done sometimes contains a fair percentage of indigotin.

Indigotin Estimation.—The indigotin is estimated by reduction of the indigotin with hydrosulphite.

REDUCING MIXTURE.

10 grammes of metabisulphite of soda.
4 ,, zinc dust.
110 c.c. of distilled water.

These are well mixed, allowed to stand for twenty to thirty minutes, then poured into a dish containing 25 grammes of slaked lime and 125 c.c. of distilled water, again stir well, and filter in a bottle. Weigh out 2 grammes of the cake to be tested on a clock glass, wash the 2 grammes into a half-litre flask with about half the reducing mixture, make up to about 350 c.c. with distilled water, and boil for thirty minutes, then add the rest of the reducing mixture, and fill up to the mark with well-boiled distilled water. Cool, and when cold transfer 100 c.c. by means of pipette into a dish, acidify with hydrochloric acid, and add a few cubic centimetres of hydrogen peroxide, boil until the indigotin has flocculated; the indigotin is then filtered through a weighed filter, washed with water till acid free, dried, and weighed.

Example:—

100 c.c. taken from the flask. Remainder 694 c.c.
Indigotin in 100 c.c. was 0·041 gramme:

$$\frac{0{\cdot}041 \quad 694}{100} = 0{\cdot}3256 \times 50 = 16{\cdot}28 \text{ per cent. indigotin.}$$

Sud cakes must always be extracted with ether before determining the indigotin, as when grease is present the results are always too high.

Recovered Greases.—The main classes from the point of view of the quantities on the market are the Yorkshire greases. These greases are recovered from the wool-scouring liquors, or from the raw wool by extraction with solvents. They are known in the trade as hard greases.

Backwash grease is obtained from the scouring of the wool after carding, and consists of a mixture of wool fat, fatty acids from the soap used in scouring, and the fatty acids, etc., from the oil used to lubricate the wool in carding. Since the great increase in the amount of brown American cotton soap used in the textile trade, the value of many backwash greases to the distiller has been very much reduced.

Extracted Skin Greases.—The largest weight of this is of American origin.

A section likely to rise in quantity is the sewage grease. If the producers would deodorise these and sell them on a basis commensurate with their actual value—say on a basis of the percentage of normal fatty acids contained, with a rebate for all oxidised fatty acids over 5 per cent.—the distiller would know what he was buying, and the seller would know exactly the commercial value of his product. There is no difficulty in the deodorising at the present time, and if these suggestions, or something like them, were carried out, no doubt further uses would be found for these greases. Almost every trade using oils and fats are making attempts at recovery, so that the number of different classes is steadily increasing.

The extreme variation in the saponifiable matter of these products is from 8 to 98 per cent.

The methods of analysis previously given will be found suitable for all classes of recovered products.

Owing to the very variable molecular weight of the fatty acids from recovered products no volumetric methods can have any claim to accuracy. Take the free fatty acids in Yorkshire greases as an example:—

Free Fatty Acids Titr. on 282.	Free Fatty Acids, Gravimetric.
16·92 per cent.	38·6 per cent.
14·63 ,,	31·36 ,,
19·76 ,,	39·30 ,,
17·56 ,,	34·74 ,,
28·20 ,,	41·56 ,,
31·73 ,,	53·32 ,,

When extracting the unsaponifiable from all wool greases, and to a greater or less extent in backwash greases, one always gets a flocculent layer between the soap solution and the petrol layer. This middle layer consists of soaps from fatty acids of high molecular weight and high melting point. A sample was collected by filtration from the soap solution of Yorkshire grease after removing the unsaponifiable, the soap was washed on the filter with absolute alcohol until the washings were colourless. The soap was then decomposed with acid, and the fatty acids shaken out with ether. This took much time owing to the very slow solubility of these fatty acids in the ether; the ether was washed with water until acid free, then the ether was distilled off and the fatty acids dried and weighed. The following results were obtained:—

Melting point of the fatty acids in capillary tube 156° F.
Molecular weight 526, determined with N/4 aqueous potash.

Free Mineral Acid in Yorkshire Greases.—Boil 20 grammes of the sample with four separate lots of distilled water, using 50 c.c. each time, unite the extracts, boil and add hydrochloric acid and barium chloride, boil for at least one hour in order to decompose any barium salts of volatile fatty acids which were extracted from the grease by the boiling water, filter off the barium sulphate, wash, ignite, and weigh. If the boiling with acid be not carefully done, the results may be up to 200 per cent. in error. The amount of free mineral acid present in these greases seldom rises above 0·5 per cent.

ENGLISH HARD GREASES.

Specific Gravity	·945 to ·965	Iodine Value of Fatty Acids	27
Unsaponifiable	28% upwards	,, ,, Unsaponifiable	47·5
Iodine Value	19 to 41	Acetyl Value	130 to 160
Reichert-Meissl Value	3·9 to 7·0	Acetyl Value of Unsaponifiable	140
Saponification Value	91 to 127	Specific Rotation	13·7
Molecular Weight of Fatty Acids	300 to 445	Oxidised Fatty Acids	3·9 to 7·5%
Water	0·6 to 30%		
Ash	0·04 to 0·45%		

BELGIAN HARD GREASES.

Specific Gravity	·9551 to ·9600	Cold Test	84 to 98° F.
Unsaponifiable	35·79 to 43·04%	Free Fatty Acids	6·70 to 15·51 as oleic

These greases are usually clean, and the water below 1·6 per cent.

FRENCH HARD GREASES.

Specific Gravity	·9408 to ·9617	Cold Test	83 to 94° F.
Unsaponifiable	28·71 to 39·60%	Free Fatty Acids	17·37 to 30·32 as oleic

GERMAN HARD GREASES.

Specific Gravity	·9484 to ·1·008	Cold Test	82 to 105° F.
Unsaponifiable	30·62 to 39·57%	Free Fatty Acids	5·29 to 34·90 as oleic

These are often dirty, and have contained up to 18 per cent. water.

BACKWASH GREASES.

Specific Gravity	·920 to ·950	Molecular Weight of Fatty Acids	260 to 345
Unsaponifiable	6 to 28%	Ash	0·01 to 0·15%
Iodine Value	21 to 87	Iodine Value of Fatty Acids	57·6
Reichert-Meissl Value	2·0	Oxidised Acids	3 to 4·5%
Saponification Value	108 to 180		

SKIN GREASES.

Specific Gravity	·9000 to ·9328	Open Flash	110 to 342° F.
Free Fatty Acids	14·8 to 45·1 as oleic	Water and Solvent	0·8 to 3·7%
Unsaponifiable	1·7 to 47·6%	Cold Test	48 to 90° F.

These are recovered by boiling with water, and also by extraction with solvents.

Sewage Greases.—With the corporations of different textile districts trying different processes, and also the varying amount of success which has attended these efforts, these greases are most variable in composition; they always contain more or less finely divided non-fatty matter, and this probably has a good deal to do with the difficulty found in some cases of getting these greases reasonably free from water. As a rule they contain water up to 15 per cent., and non-fats up to 48 per cent.

GENERAL FIGURES.

Specific Gravity	·9285 to ·9528	Iodine Value	28·7 to 35·4
Free Fatty Acids	18·7 to 62·75 as oleic	Cold Test	73 to 94° F.
Unsaponifiable	16·8 to 35 per cent.		

A commercially complete analysis of one of these sewage greases gave the following figures:—

Water	0·73 per cent.	Combined Fatty Acids	22·73, molecular weight 429
Non-Fats	7·41 ,,	Unsaponifiable	21·33 per cent.
Free Fatty Acids	45·50, molecular weight 304		

Leaving total saponifiable matter, 68·23 per cent.
Less oxidised acids, 6·83 per cent.
Finally giving 61·40 per cent. available saponifiable matter for distillation.

BLACK OIL FROM SEWAGE.

Specific Gravity	·9270 to ·9514	Water	2·5 to 3·43 per cent.
Free Fatty Acids	32·43 to 39·48 as oleic	Non-Fats	0·45 per cent.
Unsaponifiable	41·69 to 54 per cent.	Cold Test	41 to 51° F.

Printers' Grease.—This grease is recovered from the scouring liquors of the calico printer; such greases are all strongly dyed, and, as sufficient colour distils over during distillation to discolour the distillate badly, the printers' greases have not for this reason found a ready market amongst the grease distillers. The following figures were obtained from an average sample:—

Specific Gravity	·9318	Dirt	0·8 to 4·13 per cent.
Unsaponifiable	1·62 to 18·00 per cent.	Cold Test	84 to 88° F.
Water	0·17 to 4·80 per cent.		

The following process was patented in Germany for decolourising printers' grease, but does not appear to have made headway in this country. The grease is warmed up to 50 to 55° C., filtered, washed with water, next mixed with 3 to 4 per cent. of zinc dust or iron filings, and heated to 140 to 200° C. to reduce the colouring matter. The reduction is finished when 2 to 3 drops of grease in 0·1 c.c. of caustic soda, 40 Be, and 20 c.c. of water no longer give a red or violet colouration. The colouring matters are then made soluble by sulphonation of the filtered grease at a temperature of 100 to 110° C. with 30 to 40 per cent. of 1·53 specific gravity sulphuric acid, followed by washing with water to remove the soluble bodies formed by the sulphonation.

Curriers' Grease may contain fish oils, fish stearines, Yorkshire grease, recovered grease stearines, degras, paraffin wax, and mineral oils. Water and dirt should always be determined. An average sample gave :—

Specific Gravity	·9151 to ·9245	Unsaponifiable	28·72 to 71·12%
Free Fatty Acids	3·53 to 31·02% as oleic	Cold Test	81 to 117° F.

Wool Fat Fatty Acids.—The grease coming from Germany under this name is the residual grease from the manufacture of lanoline. It is usually distinguishable from ordinary greases by its smell, which is that of the solvent used in the extraction of the lanoline. From its origin it would be supposed to consist almost entirely of the free fatty acids originally present in the material extracted. The following figures will show how far this is correct. The wool fat fatty acids are characterised by a much smaller percentage of unsaponifiable matter than ordinary wool greases. The non-fats estimation should never be omitted, as the amount present frequently rises to 10 per cent.

Specific Gravity	·9432 to ·9735	Unsaponifiable	10·72 to 23·04 per cent.
Free Fatty Acids	34·90 to 55·70 as oleic	Cold Test	84 to 98° F.

A more complete analysis gave :—

Specific Gravity	·9434		Unsaponifiable	12·66 per cent.
Free Fatty Acids	66·72, mol. wt.	346	Water	0·93 ,,
Combined Fatty Acids	19·08 ,,	433	Non-Fats	1·62 ,,

The free fatty acids contained 28·18 per cent. oxidised acids, which equals 18·80 per cent. on the original grease. Molecular weight of the oxidised acids 427. The melting point of the oxidised acids in open capillary was 140° F.

The variation in the amount of unsaponifiable matter in different deliveries of grease or black oil from the same source is naturally a matter of great interest to the distiller or user of such greases. The following gives the extent of this variation. For this purpose only greases known to come straight from the maker have been taken, and the figures represent hundreds of deliveries.

Soft Greases	4·50 per cent.	Hard Greases	5·43 per cent.
Medium Greases	4·28 ,,	Black Oils	4·89 ,,

Any variation outside the above limits may be taken as fair ground for complaint.

BLACK OILS.

These are of two classes, pressed and extracted. The plain term "black oil" usually means, in the trade, an oil from 40 to 90 per cent. saponifiable matter.

Those oils called "pressed black oils" in the trade are oils from 8 to 26 per cent. saponifiable matter, and are recovered from shoddy dust, sponge cloths, engine waste, etc., by pressure.

Extracted black oils are oils from 1·5 to 25 per cent. saponifiable matter recovered from similar materials to the pressed oils, but are recovered by means of solvents, petrol being that most frequently used.

BLACK OILS.

Specific Gravity	·9020 to ·9485	Open Flash	330 to 360° F.
Free Fatty Acids	29·48 to 77·55% as oleic	Cold Test	22 to 75° F.
Unsaponifiable	7·65 to 62·74%	Iodine Value	40·1 to 81·9

The amount of matter volatile in the steam oven is not large in such samples, being usually under 2 per cent.

PRESSED BLACK OILS.

Specific Gravity	·8998 to ·9223	Open Flash	318 to 400° F.
Free Fatty Acids	1·06 to 7·05% as oleic	Cold Test	24 to 38° F.
Unsaponifiable	76·21 to 96·83%	Iodine Value	19·1
Vaporising Point	180 to 234		

These oils having a higher market value than the extracted oils, are liable to be mixed with the extracted oils. The volatile matter in pressed black oils does not rise above 3 per cent.; these oils should be practically odourless, any smell of solvents pointing to admixture with the extracted oils; this may be confirmed by the determination of the volatile at 212° F.

EXTRACTED BLACK OILS.

Specific Gravity	·8614 to ·9300	Open Flash	85 to 374° F.
Free Fatty Acids	0·7 to 10·58% as oleic	Cold Test	26 to 37° F.
Total Saponifiable	1·62 to 26%	Iodine Value	19·3 to 36
Vaporising Point	65 to 208° F.		

The matter volatile at 212° F. rises in very bad samples as high as 39 to 40 per cent., the usual range being 3 to 15 per cent. This test gives the best indication of the care used in driving off the solvent, and also tells the maximum loss one can have in working the sample.

Owing to the presence of solvent it is impossible to obtain a correct value for the amount of unsaponifiable matter in these samples. The following are figures obtained for the unsaponifiable matter in one of these oils :—

Percentage of unsaponifiable after ½ hour in steam oven	73·15 per cent.
" " 1 " " " "	68·86 "
" " 1½ " " " "	66·06 "

Therefore in every case of extracted black oils or mixtures containing them one must estimate the saponifiable instead of the unsaponifiable. The fatty acids are practically non-volatile at the temperature of the steam oven.

Extracted black oil fatty acids :—

After ½ hour in the oven	20·62 per cent.
" 1½ " " " "	20·62 "

If the sample contains any water, the result of heating the sample in the oven must be reported as water and loss.

It is frequently of interest to know whether a given sample is a natural product, or has been made by mixing black oil, mineral oil, and grease.

The ratio of the free fatty acids calculated on 282 to the total saponifiable minus the free fatty acids gives a fairly good indication of origin in all black oils over 20 per cent. saponifiable matter. In genuine black oils this ratio does not fall below 1·6. The actual ratios fall from 8·4 to 1·6, with an average just over 2. All the samples examined with a ratio below 1·5 have on further examination proved to be mixtures, and not natural black oils. In mixtures the ratio is usually below 1, and only in very exceptional cases does the ratio rise to 1·4. In mixtures the ratio varies from 0·6 to 1·4.

Viscosity of Black Oils.—The viscosity of the extracted black oils is often higher than that of the pressed oils, owing to the general presence of lubricating oils, and even of dark cylinder oils in the extracted black oils as a class.

PRESSED BLACK OILS.

Viscosity Redwood at 70° F. . . .	598 to 810
,, ,, ,, 140° F. . . .	76 to 98

EXTRACTED BLACK OILS.

Viscosity at 70° F. . .	946	643	878	731	373	380
,, 140° F. . .	106	80	75	92	70	71
Open Flash ° F. . . .	376	380	375	377	382	370

It will be seen that there is no relation between the viscosity and the flash point, which is rather surprising.

It is quite easy to remove most of the solvent by steaming with open steam; closed steam has very little effect.

Original sample open flash 250° F.
After two hours' steaming, open flash 364° F. open steam.
,, ,, ,, ,, 290° F. closed steam.

DISTILLATION OF RECOVERED PRODUCTS.

The ideal sought by the distiller of recovered products is when

$$\frac{\text{Total saponifiable matter}}{\text{Free fatty acids}} = 1.$$

Although this is never reached, there are recovered products on the market which approach quite closely this figure. In order to obtain correct figures from which to calculate the ratio, both the saponifiable and the free fatty acids must be determined either gravimetrically or both, volumetrically. The distillation is carried out with superheated steam.

The products of the distillation are:

Spirit Oil.—This is the first product to come over at the beginning of the distillation.

Gas Oil is that portion of the distillate which is too volatile to condense in the ordinary condenser.

Pale Distillate.—The middle portion of the distillation.

Still Returns, Back Ends, or Seconds.—The dark coloured distillate which comes off towards the end of the distillation.

Pitch.—The practically non-volatile portion of the grease; this is left behind in the still.

Unlike the distillation of fatty acids, the temperature at which the distillation is carried out varies with the raw material distilled. The extent to which fractionation is carried out varies with the ideas of the distiller and the nature of the products required; certain products, such as the gas oil and back ends, are usually redistilled; the amount of redistilling of other products again varies with the class of finished products required, and also with the market for which they are intended. Redistilling is carried on to a much greater extent on the Continent than in this country, a fact which accounts for the Continental products as a rule having less smell than the usual British article of the same grade.

The following table gives the results of samples taken from the distillate, and finally from the still, at half-hour intervals through the run of a still charged with brown Yorkshire grease:—

RECOVERED FROM SAMPLES TAKEN EVERY HALF HOUR THROUGHOUT DISTILLATION OF HARD GREASE.

	Specific Gravity.	Iodine Value.	Saponifiable Extracted.	Unsaponifiable Extracted.	Free Fatty Acids Extracted.	Per cent. KOH.	Fatty Acid Molecular Weight.	Samples.
1	·8659	56·6	37·45	58·73	41·88	8·34	351	20
2	·8489	58·0	30·42	64·25	35·27	8·07	282	20
3	·8439	57·0	32·08	59·95	39·79	10·3	179	35
4	·8517	53·8	36·44	55·63	42·15	13·0	157	38
5	·8703	52·0	50·72	44·44	57·68	11·0	272	54
6	·8732	47·8	49·34	41·81	60·76	14·0	198	56
7	·8941	45·0	60·85	32·64	59·13	16·8	233	61
8	·8934	43·7	66·79	30·86	69·86	14·9	230	63
9	·8954	43·4	69·62	29·47	68·29	16·5	237	63
10	·9015	39·8	70·69	28·48	67·78	14·8	267	63
11	·9064	38·8	70·34	28·81	67·64	14·2	267	65
12	·9019	38·5	65·06	28·38	67·47	13·6	271	66
13	·9039	38·6	64·03	36·24	63·25	13·2	272	67
14	·9094	39·2	58·86	38·68	64·01	14·3	265	68
15	·9111	41·5	60·69	37·51	61·34	12·7	267	69
16	·9165	41·7	56·95	37·68	61·23	12·3	258	70
17	·9145	43·9	58·56	36·74	61·35	12·4	264	71
18	·9150	44·0	58·25	39·90	61·32	11·9	274	72
19	·9199	51·3	58·88	39·48	57·94	11·4	288	73
20	·9119	53·3	55·73	42·09	57·34	13·7	287	75
21	·9157	52·5	52·24	43·96	52·80	9·4	313	78
22	·9204	52·7	49·57	46·89	57·77	9·3	298	85
23	·9170	54·5	48·14	48·93	46·45	8·5	334	93
24	·9131	53·2	46·23	53·24	48·73	7·7	416	103
25	·9259	53·8	42·60	55·49	43·65	7·3	325	108
26	·9327	52·0	45·01	56·23	43·74	6·8	375	112
27	·9361	53·7	43·91	55·88	42·54	6·3	392	117
28	·9251	48·9	45·94	51·56	46·37	6·3	410	119
29	·9289	45·4	43·32	55·54	47·70	6·4	408	122
30	·9212	43·0	44·86	53·60	51·35	6·8	404	124
31	·9172	41·2	38·47	57·66	51·34	6·9	425	125
32	·9233	41·8	51·24	48·67	50·89	6·7	465	127
	Pitch	40·2						

The first runnings of the distillation "spirit oil" are characterised by a strong smell, low specific gravity, and high volatility.

Specific Gravity	·7901 to ·8746	Open Flash	90 to 312° F.
Free Fatty Acids	11·25 to 87·83% as oleic	Cold Test	18 to 68° F.
Unsaponifiable	11·35 to 64·04%	Molecular Weight of Fatty Acids	239 to 280

The percentage of matter volatile at 212° F. rises up to 92 per cent.

Gas Oil.—The product termed gas oil in the trade is a very bad smelling body which is too volatile to condense in the condenser, which of course has to be kept hot throughout the distillation ; its figures vary between wide limits according to the material distilled; this gas oil is one of the main sources of loss to the distiller.

Specific Gravity	·9008 to ·9100	Open Flash	189 to 312° F.
Free Fatty Acids	22·79 to 71·90 as oleic	Cold Test	52 to 91° F.
Unsaponifiable	16·65 to 65·20	Molecular Weight of Fatty Acids	258 to 361

Pale Distillate.—The main product of the distillation is the pale distillate, which is suitable either for pressing or for sale as it is. The percentage obtained varies both with the raw material and the care taken during the progress of the distillation.

As recovered greases are obtained from very different sources, so the distillates vary in their nature.

Average Figures, Pale Distillate.

Specific Gravity	·8970 to ·9264	Melting Point	70 to 125° F.
Unsaponifiable	4·5 to 55 %	Cold Test	65 to 122° F.
Iodine Value	16·8 to 65	Open Flash	300 to 331° F.
Saponifiable Value	30 to 190	Molecular Weight of Fatty Acids	272 to 331

Distillates from Cotton Foots.—In order to obtain and keep a good colour these usually have to be redistilled ; the colour of the market products is almost white, and they are practically odourless.

Specific Gravity	·9163 to ·9223	Unsaponifiable	8 to 34·64%
Free Fatty Acids	64·16 to 94·47% as oleic	Melting Point	86 to 96° F.
		Cold Test	82 to 91° F.

Distillates from Continental Greases.—These are always of a good colour, and have but little smell, owing to the redistilling that is usually practised.

Specific Gravity	·8956 to ·9214	Unsaponifiable	21·60 to 53·00%
Free Fatty Acids	43·36 to 77·20% as oleic	Cold Test	71 to 127° F.
		Iodine Value	38 to 40·3

Still Returns, Back Ends, Seconds.—This last portion of the distillate is usually so dark in colour that it can only find a very limited market, and so is usually redistilled.

The colour varies from dark brown to black, and as all wool grease products have more smell the more volatile they are, the back ends of the distillate have but little smell, and of course a fairly high open flash.

Specific Gravity	·9135 to ·9291	Cold Test	68 to 135° F.
Free Fatty Acids	22·91 to 53·65% as oleic	Iodine Value	39·8 to 41·7
Unsaponifiable	30·30 to 63·27%	Molecular Weight of Fatty Acids	292 to 446
Open Flash	361 to 391		

RECOVERED GREASE OLEINES.

One of the most characteristic things about the recovered grease oleine is its peculiar smell, which always reminds one of wool. The amount of smell is variable, and at times not at all objectionable. The most reliable test chemically is the unfailing presence of the decomposition products of cholesterol. The many qualitative tests brought forward by the chemists of the German customs for the qualitative distinction of pure and adulterated wool grease oleines may be dismissed *en bloc*, as it is quite obvious that they have been based on the examination of a ridiculously inadequate supply of samples, both from the point of view of purity, and also as to the various qualities that are, at any rate, on our British market.

The viscosity of recovered oleines rises with the rise in the percentage of unsaponifiable matter in the sample.

Percentage of Unsaponifiable.	Viscosity at 70° F. Redwood.
35	195
50	465
60	660

The above figures were, of course, from pure samples.

The percentage of unsaponifiable matter in recovered grease oleines varies from 11 to 63 per cent., according to the quality of material distilled, and the extent to which fractionation has been carried out by the maker.

The specific gravity varies in the same way from ·8950 to ·9210.

The recovered oleines of Continental origin are most noticeable for absence of smell and for good fluidity.

Many of the recovered oleines on the market are adulterated, as may be seen from the figures. If the free fatty acids be titrated as oleic, then the difference between the total saponifiable matter and the titration should not exceed 7·5 per cent.; if this figure is exceeded, it will always be found that an addition of neutral oil has been made.

The specific gravity rises with the increase in the percentage of unsaponifiable matter, but except in the case of oleines with over 55 per cent. unsaponifiable, the specific gravity is always below ·920. The specific temperature reaction is always low, and the rise of temperature in Mackey's tester is never above 210° in two hours. The iodine value is always below 90 in genuine samples. There are many oils on the market which are sold as wool oils, and which cause no confusion if sold under that name, but unfortunately they are often marketed as oleines; such oils contain a low percentage of free fatty acids, a high percentage of combined fatty acids, and are generally a mixture of oleines and vegetable, or more often of fish oils and resin, and on this account have a high iodine value, and also a high specific temperature reaction.

The figures given below show that many oils sold as recovered oleines are far from their description.

The samples given under each heading are all from the same source.

RECOVERED GREASE OLEINES.

Test.	Specific Gravity.	Free Fatty Acids as Oleic.	Unsaponifiable.	Iodine Value.	Open Flash.	Cold Test.
Per cent.		Per cent.				
70	·8996–·9060	66-71	27–31	64–88	330–342	32–57
70	·9018–·9140	49·39–74·03	21·82–32·68	...	317–347	43–52
70	·9067–·9201	26·79–29·96	30·25–54·98	...	352	45–48
70	·9055–·9081	64·51–67·33	29·89–32·78	...	350	50–57
70	·8972–·9200	49–71·21	22·7–29·1	...	...	41–52
50	·9131–·9168	45–48·6	48·6–51·7	...	330–336	48–53
50	·9096–·9152	38·8–44·4	51·6–61	54·9	335–347	43–50
50	·8996–·9250	40·9–52·9	45·1–54·2	50–58·4	317–347	36–61
50	·9052–·9133	44·8–51·8	47·8–51·8	53·4	316–334	54–62
50	·9106–·9142	47·24–51·82	46·84–49·73	57–61	336–356	51–57
40	·9116	29·3	68·3	52·1	323	59
40	·9140–·9218	35·25–37·32	58·33–61·99	51–56·5	334–358	49–56

Oleine from Recovered Cotton Products.—In order to obtain products in line with the usual run of recovered oleines from other sources the cotton oleines require filtering to remove stearine.

	Unfiltered.	Filtered.
Specific Gravity . .	·9010 to ·9239	·9040 to ·9051
Free Fatty Acids . .	91·3 to 98·70 as oleic	80·02 to 97·29 per cent. as oleic
Unsaponifiable . .	1·3 to 8·7 per cent.	3·73 to 18·16 per cent.
Iodine Value . . .	...	104·4
Open Flash . . .	343° F.	347 to 353° F.
Cold Test . . .	64 to 76° F.	39 to 54° F.
Refractive Index . .	...	1·4705 to 1·4715.

The percentage of saponifiable matter is often brought down to 70 per cent. or 50 per cent. before marketing; this is usually done by the addition of mineral oils.

Recovered Oleines of Foreign Origin.

Specific Gravity . .	·8977 to ·9120	Iodine Value . .	61·2 to 64·6
Free Fatty Acids . .	44·42 to 62·04% as oleic	Cold Test . . .	45 to 58° F.
Unsaponifiable . .	38·71 to 55·39%	Refractive Index . .	1·4735 to 1·4881
Open Flash . . .	335 to 352° F.		

DRY CLEANERS RESIDUES.

These always contain solvent and soap, and sometimes water and dirt.

When water is present, the water and loss of solvent may be estimated together by drying in the oven and the result reported as water and solvent.

Solvent rises to 55 per cent., Dirt rises to 5 per cent.

Owing to the presence of solvent the open flash of these samples is usually below 200° F. The oil left after removing solvent usually tests about 79 per cent. saponifiable.

RECOVERED GREASE STEARINES.

The colour of these stearines varies from paper white to dark brown. Average samples give :—

Specific Gravity ·9185 to ·9709.
Unsaponifiable 0·5 to 45 per cent.
Iodine Value 11 to 41 in wool fat products.
Iodine Value rises to 85 from other recovered products.
Saponification Value 51·8 to 160 from wool fat products.
Saponification up to 195 from other products.
Melting Point 105 to 150° F. from wool fat products.
Melting Point up to 128 from other products.
Iodine Value of the Unsaponifiable 47 to 70 from wool fat products.
Molecular Weight of Fatty Acids 260 to 330 from wool fat products.
Iodine Value of the Fatty Acids 26·2 to 29·4 from wool fat products.

The chief use of the recovered stearines is in the leather trade. The amount of stearine from recovered products that is good enough for the candle-maker is very small.

The practice of mixing paraffin wax with the various stearines has grown to very large dimensions during the past few years. The following figures are the result of an analysis of such a mixture, made with the view of arriving at a match for the sample :—

Original Sample.

Free Fatty Acids	59·57% as oleic	Melting Point of Sample	100° F.
Unsaponifiable	46·35%	Molecular Weight of Fatty Acids	272
Total Saponifiable	53·65%		

On boiling out the unsaponifiable with acetic anhydride, 74 per cent. of insoluble hydrocarbon was found, having a melting point of 74° F. The softest white scale on the market is the wax used by the match-makers, this wax having a minimum melting point of 102° F., therefore the hydrocarbons of melting point 74° F. must be a mixture of scale and mineral oil. This gives 35 per cent. wax and oil added to the original stearine, in which we can calculate 11·5 per cent. unsaponifiable, finally finding that the stearine used had a melting point of 100° F., and was 85·5 saponifiable.

A mixture was made with such a stearine, scale, and mineral oil, which mixture gave similar figures to the original sample.

White Stearine from Black Oils.

Free Fatty Acids	100 as oleic	Molecular Weight	270 to 280
Melting Point	106 to 120° F.	Unsaponifiable	up to 13%
Iodine Value	26·1		

100 to 105 Pale Stearine from Black Oils.

Specific Gravity	·9185	Iodine Value of Unsaponifiable	47·2 to 49·8
Free Fatty Acids	80 to 91% as oleic	Iodine Value of Fatty Acids	26·2 to 29·4
Unsaponifiable	13·42 to 20·69%	Molecular Weight of Fatty Acids	266 to 274
Melting Point	99 to 108° F.	Melting Point of Fatty Acids	108 to 109° F.
Iodine Value	32·9 to 34·8		

110 TO 112 PALE STEARINE.

Specific Gravity	·9265	Iodine Value	26·8 to 31·4
Free Fatty Acids	74 to 79% as oleic	Molecular Weight of Fatty Acids	...
Unsaponifiable	20 to 27%		
Melting Point	108 to 113° F.		

95 TO 105 STEARINE FROM YORKSHIRE GREASES.

Free Fatty Acids	73 to 79% as oleic	Iodine Value	24·4 to 38·9
Unsaponifiable	20 to 28%	Molecular Weight of Fatty Acids	288 to 290
Melting Point	95 to 103° F.		

Yellow Stearines from Yorkshire Greases.—These vary with the raw material from which they are obtained and the season of the year at which they are made, which has a considerable influence on the melting point of the stearine.

Specific Gravity	·9300	Melting Point	108 to 125° F.
Free Fatty Acids	58 to 66% as oleic	Iodine Value	31·8 to 40·1
Unsaponifiable	19 to 34%	Molecular Weight	274 to 330

HOT-PRESSED YELLOW STEARINE.

Specific Gravity	·9700	Unsaponifiable	32 to 35%
Free Fatty Acids	45 to 49% as oleic	Melting Point	130 to 145° F.

CHOLESTERINE WAX.	BRITISH.	FRENCH.	GERMAN.
Free Fatty Acids	19·4 to 44·4	46·5 to 46·8	43·7 to 45·8
Unsaponifiable	...	45·5	...
Melting Point	129 to 150° F.	129 to 130° F.	129 to 135° F.
Iodine Value	34·4 to 37·5	41·4	...

COTTON STEARINES.

Unsaponifiable	0·75 to 16%
Melting Point	96 to 127° F.
Molecular Weight	291

Stearines derived from wool fat may be distinguished from those of any other origin by dissolving in petrol-ether, ·64 specific gravity, warming, if necessary, after cooling; if wool fat products are present, solid acids of high melting point will separate up to 160° F. melting point.

EMULSIONS AND EMULSION OILS.

These are perhaps best classed together, for the only difference between them is the variation in the percentage of water they contain.

The usual constituents are: water, oils or greases of very varied origin, hard or soft soaps, ammonia, phenol, stearamide, and extracts usually of a gelatinous nature, such as Irish moss, etc. In addition to the above, the emulsion oils may contain up to 5 per cent. of alcohol.

It is advisable to make a preliminary examination by heating a few cubic centimetres of the sample—whether an emulsion or an emulsion oil—in a test-tube, when both ammonia and alcohol if present will be detected by the smell.

Another portion should be boiled in a test-tube with strong hydrochloric acid until the fatty layer on the top is quite clear; if phenol is present it will also be detected by the smell, and any sulphonated oil will be decomposed; then if the acid layer is pipetted off, diluted with water, and barium chloride solution added, a white precipitate of barium sulphate will indicate presence of sulphonated oils of some description.

A further sample is boiled until all the ammonia if present is boiled off, then caustic soda is added, and the contents of the tube again boiled; if ammonia is again given off, the presence of stearamide is proved.

The following will be found to be a fairly general method of examination:—

Alcohol.—Take 20 to 30 grammes of the sample and mix with its own weight of water in a 300 c.c. flask, then distil off three-fourths of the total; the specific gravity of the distillate is taken in a specific gravity bottle at 60° F., and the alcohol content calculated from the density tables.

Water.—Weigh out accurately into a beaker containing a glass rod about 10 grammes of the sample, and dry in the water oven until the loss does not exceed 2 milligrammes per hour; when calculating out the water, any alcohol, ammonia, or both if present, must be deducted from the loss of weight on drying in order to obtain the correct percentage of water.

Ammonia.—Ten grammes of the sample are weighed into a flask, diluted with 100 c.c. of water, and excess of caustic potash added; the flask is connected with a steam generator and a bulb receiver containing 25 c.c. of N/2 hydrochloric acid, then distil off three-fourths of the whole; the acid in the receiver is titrated back, and the amount of ammonia calculated.

Total Alkali.—The emulsion oils very often contain soap, either added as such, or formed during the making of the oil; they are also often cleared with ammonia at the end of the process; the question which alkali was used for the soap is best answered by the pocket spectroscope.

About 10 grammes of the sample are weighed into a dish, diluted with about 100 c.c. of water, and titrated with N/2 hydrochloric acid, using methyl orange as indicator; in order to obtain the potash or soda, any ammonia present must be deducted.

Oil.—The residue left in the beaker from the water estimation is next extracted with ether (if exact results are required the ether must be dry and alcohol free). The ether is filtered into a weighed fat flask, taking care that as little as possible of the insoluble portion is allowed to get on to the filter. When the residue (if any) on the filter is fat free, and the filter washed with ether until fat free, the filter is kept on one side for the soap estimation which follows. The ether filtrate is distilled off, and the oil in the flask dried in the oven, cooled, and weighed. The oil in the flask is used for the analysis of the oil.

Soap.—The residue in the beaker is boiled out with absolute alcohol at least four times, or more if soda soaps are present, and the alcohol filtered through the filter put aside from the oil estimation; the filtrate is collected in a weighed flask, the alcohol distilled off, and the residual soap dried in the oven, cooled in a desiccator, and weighed, the soap being put aside for further examination.

When ammonia is the only alkali present it is all driven off during the drying of the sample, and of course leaves behind its equivalent amount of free fatty acids, which must be deducted from the amount of free fatty acid found on titrating the oil separated from the sample.

If any residue insoluble in alcohol is found it is usually Irish moss extract, which is soluble in water, dilute acids, and alkalis.

In the highest class of emulsions the saponifiable matter is often olive oil, either pure or adulterated, and from this the oil ranges down to recovered greases in the case of emulsions for batching jute. In many lower-class emulsions the amount of mineral oil present is up to 75 per cent. of the total oil in the sample. These large variations require a fairly complete analysis of the oil if the figures are to be of any use in matching the sample. If the examination be carried out on the lines given in section under "Chemical Examination," there should not be much difficulty in obtaining the necessary information.

Phenol is only a very rare constituent, although it has very good emulsifying power.

SOAPS.

The analysis of soap has been fully treated so often that there is no need to take up any space with this; below are a few results of special classes.

Brown American Cotton Soaps.—These are made from cotton foots, and are in extensive use in the textile trade. The foots used always contain non-fatty matter, and in some cases resin is added to the foots.

These foots contain unsaponifiable matter up to 5 per cent., and the non-fats rise to 9 per cent.

The percentage of fatty acids in these soaps varies from 58 to 75 per cent.

Many of these cotton soaps contain both free fatty acids and free alkali at the same time, which shows very careless manufacture.

A sample of the stock from which these brown cotton soaps are made yielded 70 per cent. of fat fit for soap making; this fat contained 55 per cent. of free fatty acids.

Liquid Soluble Soaps.—These were originally made from castor oil, but latterly have been made from mixtures of various oils and resin, and also from cocoanut oil.

Some samples are almost neutral, and others contain a large excess of alkali.

The original liquid soaps were from castor oil, and contained 15 per cent. of fatty acids; the samples from resin mixtures usually contain 2 to 3 per cent. more fatty acids; in order to obtain a similar consistence, the cocoanut oil samples may contain up to 35 per cent. of fatty acids.

The analysis of these samples is carried out as described under Emulsions.

BROWN WOOL OILS.

These are usually mixtures of recovered wool grease and mineral oil, but contain sometimes a certain percentage of fish oil, recovered grease oleine, resin. Their specific gravity varies from ·900 to ·925, and the saponifiable matter varies from 4 to 50 per cent., with a usual run of from 20 to 30 per cent. saponifiable matter.

Water is always present, varying from 1 to 12 per cent. A trace of potassium carbonate usually accompanying a water percentage of 5 or over, this potash is easily detected with the pocket spectroscope.

Water can only be determined with accuracy by distillation with xylol, but simple driving off over an Argand burner is useful as a works check.

Free Fatty Acids may be determined by titration on oleic acid, but gravimetric estimation is again the only accurate method.

Saponifiable Matter.—The mineral oil used in these brown oils is often of low quality, and so volatile that one must determine the saponifiable direct instead of the unsaponifiable, in the same way as the extracted black oils.

PITCH.

From distillation of fatty acids, wool grease, and other recovered fats. These pitches are commercially divided into three classes, hard, medium, and soft, which terms have reference to the melting point of the sample; but in some cases it is a difficult matter to decide to which class a given sample belongs, and up to the present, unlike the coal-tar pitches, no limits have yet been fixed.

The solubility of these pitches in the usual solvents is very variable, particularly in the case of the fatty acid pitches, so much so, that one sample of pitch from a given fatty acid is almost entirely soluble in a solvent that will not dissolve 5 per cent. of another sample from the same fatty acids; this solubility, or lack of solubility, depends on the point at which the distillation was stopped. The presence of a greater or less amount of albuminous matter in the fatty acids distilled has a very great effect on the properties of the pitch left behind on distillation.

The analysis of these pitches is still in a very rudimentary state, and, with the exception of a certain amount of work done in Germany on wool grease pitches, the published information is almost nil.

Specific Gravity.—A bit of the sample is dropped into a dish of water, in which it will sink or float according to its specific gravity.

If the sample sinks to the bottom, a pea-sized piece is placed in a mixture of alcohol and water, varying the amounts of alcohol and water until the sample neither sinks to the bottom nor floats on the top, but swims about in suspension, care being taken to free the sample from air-bubbles; the specific gravity of the alcohol is then taken in the specific gravity bottle in the usual way, the result being the specific gravity of the sample taken.

If the sample floats on the water in the dish, a piece of the sample the size of a pea is placed in a beaker of water, and common salt solution added until the sample remains suspended, when the specific gravity is taken as before.

Volatile Matter.—Weigh as near as possible 3 grammes of the sample into a platinum dish and heat over a Bunsen burner until the contents of the dish cease fuming, cool, and weigh; the loss of weight gives the volatile matter. In order to obtain comparable results it is essential that similar weights be taken and the heating be as rapid as possible, otherwise widely different results will be obtained from the same sample on repeating..

Ash.—Continue heating the residue from the volatile matter until all the carbonaceous matter is burned away, cool, and weigh.

Free Fatty Acids.—The presence of free fatty acids in all pitches from the distillation of fatty acids, whether pure or recovered, gives us the most rapid means of distinction between these pitches and the pitches from the distillation of mineral oils.

The acidity of fatty acids and recovered grease pitches is never below, and only in very rare cases falls as low as, 1 per cent. as oleic acid, and, on the other hand, the acidity of mineral oil pitches is always below 0·5 per cent.

The acidity is determined in the usual way by dissolving 2 grammes of the sample in a mixture of hot motor spirit and alcohol. In the case of some fatty acid pitches solution is very slow, and considerable patience is required along with much shaking; the solution is then titrated with N/2 potash and phenolphthalein.

Saponifiable Matter.—The following is the only method applicable to all samples, and has stood the test of regular works use:—

About 2 grammes of the sample are weighed into a 300 c.c. flask and saponified with 25 c.c. alcoholic potash; after saponification the flask and contents are cooled under the tap, and the soap solution filtered into a separator; the residue is saponified in the same way twice more, cooling and filtering through the same paper each time; the filter is then washed well with alcoholic potash, allowing the washings to run into the separator. The soap solution and washings are now diluted with 30 c.c. of water, and the whole shaken out with petrol, and the petrol washed in the usual way. Shaking out and washing of the petrol is continued until the petrol extract remains colourless. The petrol extracts can be run into a weighed flask, the petrol distilled off, and the residual unsaponifiable matter dried and weighed if required; but as there is generally more or less insoluble residue from the saponification, the result does not appear to have much value. The soap solution is evaporated down on the steam bath until alcohol free, the washings are then added, and the whole decomposed with acid, boiled until the fatty layer is quite clear, cooled under the tap, poured into a separator, and shaken out with ether meth.; after separation has taken place the acid layer is run off, and the ether washed with water until acid free; the ether extraction of the soap solution is repeated, the two ether extracts united in a weighed flask, the ether distilled off, and the residual fatty acids dried in the oven, cooled, and weighed; the flask containing the fatty acids is put aside for further examination if required.

German Customs Method.—This is only applicable to wool grease pitch.

Two grammes of the sample are weighed into a flask and dissolved in 50 c.c. of ether, the solution is then precipitated with 50 c.c. of absolute alcohol.

The flask and contents are allowed to stand overnight, filtered through a double filter, and the filter washed clean with alcohol-ether mixture (1 to 1 by volume). The filtrate and washings are then saponified by boiling with 30 c.c. of N/1 alcoholic potash for one and a half hours under reflux, cooled, and shaken out four times with petrol to remove unsaponifiable matter, the soap solution evaporated on the steam bath until alcohol free, the soap dissolved up in the washings, the solution decomposed with acid, shaken out twice with ether, the ether washed with water until acid free, run into a weighed flask, the ether distilled off, and the saponifiable matter in the flask dried in the oven, cooled, and weighed.

A sample of wool grease pitch gave 12·59 per cent. saponifiable by first method. The same sample gave 11·95 per cent. saponifiable by second method.

To see whether the alcohol-ether method had left any saponifiable matter in the residue this was dissolved up in carbon disulphide, 25 c.c. of alcoholic potash added, and left to stand for twenty-four hours, with occasional shaking, after which time it was treated like the alcohol-ether filtrate. The saponifiable matter extracted from the residue was 0·65 per cent., and 11·95 plus 0·65 equals 12·60 per cent., a result which is in close agreement with that of the method first described.

A sample of cotton pitch gave 12·18 per cent. saponifiable by first method. The same sample gave 7·17 per cent. saponifiable by second method, and with some samples of fatty acid pitch the difference would be much greater.

Melting Point.—This varies from 80 to 180° F. The open capillary and the Kraemer-Sarnow methods are the only ones of any use, and even then, with some fatty acid pitches, neither may be applicable.

Iodine Value.—Wool grease and mineral oil pitches are completely soluble in chloroform, and so give no trouble; but many fatty acid pitches and cotton pitches are only slightly soluble in most solvents, and in such cases it is not possible to determine the iodine value at all. The following have been tried in the attempt to find a solvent for these pitches: acetone, pyridine, chloroform, ether, carbon disulphide, carbon tetrachloride, absolute alcohol, amyl alcohol, glacial acetic acid, benzol, xylol, acetic anhydride, petrol-ether, paraffin, ethyl acetate, turpentine, trichlorethylene, perchlorethylene, tetrachlorethane, pentachlorethane.

Detection of Mineral Oil Pitch in Fatty Pitches.—The following method has been given by the German customs for the detection of mineral oil pitch in fatty pitches, but although the method is given for fatty pitches generally, the fact that the method requires the sample to be soluble in benzol makes this method only applicable to wool grease pitches.

The Mercuric Bromide Test.—The sulphur compounds in asphaltum and mineral oils give with mercuric bromide double salts which are soluble in warm chloroform or benzol. The sulphur compounds in fatty pitches rise from impurities or from the use of sulphuric acid after autoclaving, and yield no double salts with mercuric bromide.

Dissolve 10 grammes of pitch in 250 c.c. of benzol, warming if necessary, cool, and add 30 c.c. of alcoholic potash (to remove the fatty acids contained in the sample), shake, and then dilute with 200 c.c. of 96 per cent. alcohol. After standing for a short time the alcohol solution, which must still be alkaline, is poured off, and the pitchy residue in the flask washed once with alcohol, and dried until alcohol free. After this preparation the residual pitch in the flask is dissolved in 100 c.c. of ether, warming if necessary. The residue will be found to be much more soluble than the original pitch, due to the removal of the fatty acids, and a few pieces of ignited calcium chloride are added to remove water; when all is dissolved, or at least finely divided, allow to settle, and filter through a folded filter; the filtrate is collected in a boiling tube; to this add 20 c.c. of mercuric bromide solution (5 grammes of mercuric bromide in 250 c.c. of ether), and allow the tube to stand overnight. The precipitate, if any, is filtered off and washed with ether, and then dissolved off the filter with warm benzol. Any separated bromide is left on the filter undissolved. After evaporating off the benzol the double salt is left as a dark brown to black brittle mass. In order to prove that a double salt has actually been formed, pour a few cubic centimetres of nitric acid over the mass, and after the action has subsided evaporate on the water bath, take up the residue with water, and test the aqueous solution for sulphuric acid with barium chloride, silver nitrate for bromine, and ammonia and ammonium sulphide for mercury. This process is said to be able to detect 20 per cent. of mineral oil pitch in a mixture.

Free Carbon in Pitches.—Free carbon is only found in pitches that have been driven nearly down to coke, or have been heated after leaving the still, and consequently is but rarely found. Therefore it need only be looked for when a pitch sample is sufficiently brittle to crumble up when rubbed between the finger and thumb.

Estimation.—Weigh 3 to 5 grammes of the sample into a flask and extract with pure CS_2 until nothing further dissolves; when this point is reached, the carbon disulphide will remain quite colourless; the carbon disulphide solution is filtered through a dried and weighed filter paper, and the filter washed with carbon disulphide until clean. The filter is then dried and weighed. The residue on the filter consists of any free carbon present and the whole of the ash in the sample. The residue is ignited and the ash weighed. Then the weight of the carbon disulphide residue minus the ash left on ignition gives the free carbon in the weight of the sample taken.

ANALYTICAL FIGURES, WOOL GREASE PITCH.

Specific Gravity, from 0·97 to over 1.
Melting Point, from 90 to 160° F.
Volatile matter, 65 to 92%, with 75% as a fair average.
Ash, 0·5 to 5·5%.
Free Fatty Acids, 0·75 to 15% as oleic, with 6% a fair average.
Saponifiable matter, from 7% in hard samples to 30% in very soft samples.
Iodine Value, 35 to 45; the softer the sample, the higher the iodine value.
Molecular Weight of Normal Fatty Acids about 440.
Oxidised Acids, up to 25%.

Soluble in carbon disulphide and chloroform with the exception of the ash.

A German sample gave the following figures:—

Specific Gravity	·9787	Free Fatty Acids	16·92% as oleic
Volatile	79·33%	Total Saponifiable	16·99%
Ash	1·71%		

The saponifiable contains—
76·89% Normal Fatty Acids, molecular weight 439.
23·21% oxidised Fatty Acids.

COTTON PITCH.

Specific Gravity, usually 1 or over.
Volatile matter, 69 to 75%.
Ash, 2·11 to 4·5%.
Free Fatty Acids, 0·7 to 9%.
Saponifiable matter, 12 to 50%; the softer the sample, the higher the saponifiable.
Sulphur, about 1%.
Melting Point, very variable.
Iodine Value, in most cases no solvent can be found.

94·5 to 97% soluble in carbon disulphide in the case of ordinary samples, to a few per cent. only in the so-called rubber pitches.

FATTY ACID PITCH.

Specific Gravity, usually 1 or over.
Volatile matter, 70 to 80 per cent.
Ash, up to 7 per cent., varying with the care taken in decomposing the fatty acids.
Free Fatty Acids, 5·6 to 45 per cent. ; the general rule is, the higher the free fatty acids the softer the sample, but there are exceptions. For example :—
Softer sample, 18·19 per cent. free fatty acids.
Harder sample, 29·11 per cent. free fatty acids.
Saponifiable matter, 15 to 90 per cent.; the softer the sample, the higher the saponifiable.
Iodine Value (like the cotton pitch) in most cases, no solvent can be found.

A more complete analysis of a sample of soft fatty acid pitch gave :—

Specific Gravity, 1·0106 at 60° F. Free Fatty Acids, 18·19% as oleic. Saponifiable matter, 89·33%. Unsaponifiable matter, 6·17%. Insoluble in alcoholic potash, 4·60% by difference.	The Fatty Acids of this sample contained— Normal Fatty Acids, 62·10%, molecular weight 359. Oxidised Acids, 38·06%, molecular weight 381.

Mineral Oil Pitch.—All mineral oil pitches contain a certain amount of solid hydrocarbons, which may be estimated by Richardson's method as follows :—Five grammes of the sample are weighed into a flask and shaken with 100 c.c. of petrol-ether 0·64 sp. gr. and let stand overnight; the solution is then filtered into a separator, and the filter washed with petrol-ether until clean. The filtrate and washings in the separator are shaken out with concentrated sulphuric acid, using 5 c.c. each time until the acid remains colourless; usually about twelve treatments with acid are required. The petrol layer is next washed with water until acid free, the petrol run into a weighed flask, the petrol distilled off, and the residue dried and weighed. In a particular case this residue was 5 per cent., and was quite soft. The residue is dissolved in alcohol-ether (1 to 1 by volume) and let stand at 32° F. to separate the paraffin. The paraffin is filtered off and washed with the alcohol-ether mixture, dried and weighed. In the sample taken the hard paraffin amounted to 1·66 per cent. on the original pitch.

MINERAL OIL PITCH.

Melting Point— Russian soft, 109° F. Kraemer & Sarnow ,, medium, 156 ,, ,, ,, ,, hard, 178 ,, ,, ,, Volatile matter, 85 to 92% Ash, generally below 0·1% Free Fatty Acids, always below 0·5% as oleic	Ether soluble, 70 to 80% Benzol soluble, about 90% Iodine Value ... American 130° F. M.P., 31·2 Kansas ,, 180 ,, M.P., 42·7 Pennsylvania Russian 150 ,, M.P., 56·1

MINERAL OILS.

Leaving out the light spirit and lamp oils, the chief varieties and origins are :—

American, Kansas . .	red oils.
,, Mexican .	spindle oil 895 to residuum 985.
,, Pennsylvania	mineral colza to residuum 935.
,, Texas . .	915 spindle to residuum 935 to 950.
Roumanian	886 ,, ,, 935 to 945.
Russian	885 ,, ,, 910 to 912 from kerosene.
	,, ,, 930 to 935 ,, lubricating oil.
Scotch	from mineral colza to 905 lubricating oil.

Appearance.—All grades, even when the colour is black, should be quite clear and bright. The chief cause of turbidity is the presence of a small amount of water; if more than 0·1 per cent. of water is present, small bubbles of water can be seen in the sample if the oil is examined with a good pocket lens; on heating a few cubic centimetres of the oil in a test-tube until no more bubbles rise, the oil will remain bright on cooling if the turbidity was due to water.

Turbidity due to insufficient washing after the soda treatment during refining. Five c.c. of the sample is boiled with 5 c.c. of water in a test-tube and put aside to settle out again. If the aqueous layer is milky after separating, the oil has not been properly washed; this fault is, with the exception of Scotch, Galician, and heavy Texas oils, not often met with at the present time.

Colour.—This can usually be judged quite near enough with the eye, and is only of importance in the case of white and half-white oils. White oils should be as colourless as distilled water, and quite free from fluorescence; a sample showing any colour is to be classed as off-colour, but of course what is off-colour for a white oil would be described as a good half-white oil.

When the colour is darker than usual for a given grade of oil, it is generally caused by the refiner heating the oil and blowing air through until the oil is dry and clear; this is sometimes done after the soda treatment instead of the usual water washing; during the blowing the soda compounds present go into solution in the oil, which is left quite clear but darker in colour than would be the case if the oil had been properly washed; the amount of ash in such samples is always higher than usual. In the refining of Texas oils such persistent emulsions are formed during the soda treatment that it is almost a commercial impossibility to separate them, and in such cases the only method open to the refiner is the heating and air blowing described above.

When oil turns darker on keeping, which occurs chiefly with Scotch oils and the lighter Galician oils, it is due to insufficient soda treatment; on warming such oils with caustic soda solution a separation of more or less soda tar will take place.

Smell.—Good qualities of both American and Russian oils have the least smell, and the lighter Scotch, Galician, and Roumanian oils the most. Crude, fuel, grease-making oils, and residuum are usually strong in smell, the chief exception being the Russian residuum from the kerosene stills.

Specific Gravity :—		American residuum	to ·980
American refined and distilled oils—		Galician refined	to ·919
Kansas	up to ·925	,, black	to ·945
Mexican	up to ·920	Roumanian residuum	to ·950
Pennsylvania	to ·925	Russian refined	to ·917
Texas	to ·950	,, residuum	to ·930
American crude and fuel oils	to ·950		

For a given specific gravity Scotch and Galician oils have the lowest viscosity, American are intermediate, and Russian oils have the highest viscosity.

Refractive Index.—This is of considerable importance, as, with the exception of the specific gravity, the refractive index is the only additive figure we possess.

Optical Activity.—Mineral oils from all sources are optically active, but as the rotation is so small, it is of no commercial interest; still it throws some light on the question of origin.

Vapourising Point.—The temperature at which the oil when heated in an open vessel first gives off visible vapour. This temperature is generally from 120 to 180° F. below the open flash point of the sample.

Open Flash Point.—The temperature at which the first blue flame runs completely round the dish.

Fire Point.—The temperature at which the oil in the dish will continue to burn when the flash light is taken away.

Coke in Mineral Oils.—Determined by heating 4 to 5 grammes of the oil in a platinum dish with a luminous Argand flame until the residue does not fume any more. The residue is then cooled and weighed.

If concordant results are to be obtained, it is essential that nearly the same quantity be taken each time, and that the heating be carried out as rapidly as can be done without allowing the oil to boil and spit.

Engler states that the coke in distilled oils should not exceed 3 per cent., and in refined oils should not be above 7 per cent., but he gives no limits for filtered and dark cylinder oils.

Oil.	Percentage of Coke.
Scotch, 885 oil	2·29
American, 865 pale	2·22
,, 885 ,,	3·30
,, 895 ,,	1·85
,, 900/907 ,,	5·90
,, 912/915 ,,	6·33
,, 912/915 red	5·44 to 6·32
,, Texas, 940/945 red	5·16
Russian, 895	1·07
,, 907	0·81
American dark cylinder oils	4·72 to 15·30
,, filtered cylinder oils, fluid	10·23 to 10·89
,, ,, ,, solid	5·29 to 10·89
White Ceresin	1·10
,, Petrol jelly	3·18
Yellow Petrol jelly	3·82 to 5·91
,, Petrolatum	7·45 to 11·13

In view of the general addition of a small percentage of fatty oils to mineral oil intended for the lubrication of internal combustion engines the effect of this addition on the coke is interesting. The effect is to lower the amount of coke formed, and presumably to lower the amount of carbonising in the cylinder of the engine.

A gas-engine oil containing 5 per cent. of fatty oil gave 4·95 per cent. coke. The same oil without the fatty oil gave 7 per cent. of coke.

Ash in Mineral Oils.—Best determined by igniting the residue from the coke estimation.

Oil.	Percentage of Ash.
American, 885 spindle	0·12
,, Texas, 935/940	0·22 to 0·24
,, dark cylinder oils	traces to 0·27
White Ceresin	traces

Resin in Mineral Oils.—Resins do not occur in mineral oils at present on the market with the exception of the Texas oils of high specific gravity.

Five grammes of the oil are weighed into a flask, and 25 c.c. of N/1 alcoholic potash added, the mixture boiled under reflux for thirty minutes. The unchanged oil is shaken out with petrol three times, the alcohol solution and washings decomposed with acid and shaken out in a separator with ether meth. twice, the ether washed with water until acid free, run into a weighed flask, the ether distilled off, and the residue dried in the oven and weighed. Two samples of red Texas oils gave 2·13 per cent. and 1·63 per cent.; the resins were in both cases solid but tacky, and were not further examined.

IODINE VALUES.

American mineral colza	2·5 to 8·0	American high cold test, filtered cylinder	6·9 to 10·3
,, 865 pale neutral	8·8 to 11·2	,, dark cylinder oils *	11·3 to 17·7
,, 885 to 890 neutral	12·4	,, low flash black mineral oils	13·1 to 19·3
,, 880/885 pale	10·4	Galician 885 pale	13·2
,, 885/890 ,,	15·5 to 18·4	,, 895 ,,	10·4
,, 895 ,,	6·7	,, 905 ,,	6·1
,, 900/907 ,,	9·7 to 11·7	,, 915 ,,	8·9
,, 905 ,,	8·4 to 11·1	Roumanian residuum	17·8
,, 912/915 ,,	7·9 to 8·5	Russian 895 pale	2·6 to 3·0
,, red 912/915	10·7 to 15·3	,, 907 ,,	3·0 to 8·5
,, ,, 925	22·1	,, 912/915 cylinder	10·0
,, Texas, pale 925	9·3	,, 910/912 residuum	6·9
,, ,, red 930/935	12·4	Scotch 865	41·6
,, ,, ,, 940/945	12·9	,, 885	20·2
,, low cold test, filtered cylinder	8·8 to 13·3		

* The iodine value of these dark cylinder oils rises with the specific gravity.

The nitration and formolite processes which follow were brought forward some time ago, and are given here because there does not seem to have been many attempts made at confirmation or otherwise. The nitration process the writer has not had the opportunity to try, but has made a few determinations with the formolite process.

Nitration.—Ten c.c. of the sample are dissolved in 10 c.c. of light petrol, and the solution added drop by drop to 30 c.c. of fuming nitric acid (sp. gr. 1·52) cooled to −10° C.; the addition of the solution must take thirty minutes. The temperature of −10° C. is best kept by immersing the vessel in a 15 per cent. salt solution, which is cooled with ice and salt. After the solution is all dropped in, 50 c.c. of cooled ordinary nitric acid is added, and the mixture poured into a separator. The acid layer is run on to ice, when the nitration products deposit as a yellow precipitate; this is filtered off, washed free from acid, and dried at laboratory temperature. The petrol layer contains paraffins, naphthenes, and polynaphthenes, and is washed with water and then with alkali until acid free, and again with water until neutral; the petrol is run into a weighed flask, the petrol distilled off, and the residue dried and weighed. There is always a slight middle layer insoluble in water, the weight of which is to be added to that of the nitro bodies.

The refractive index of the oil recovered from the nitro bodies is in all cases lower than that of the original oil.

Formolite Reaction was first put forward by Nastukoff in 1904, who stated that the proportion of unsaturated hydrocarbons could be obtained by multiplying the formolite value by four-fifths. In 1911 Marcusson stated that the formolite value estimated the unsaturated aromatic and cyclic hydrocarbons in these oils, and he showed that the iodine value of the unacted-on oil was decidedly lower than the original oil. If the percentage of the formolite precipitate depended upon the amount of unsaturated hydrocarbons present, as shown by the iodine value, the formolite value should rise with rising iodine value, but the table given below does not show any such relation, so that it appears as though a considerable amount of work will have to be done in this direction before we shall get anything definite.

Formolite Value, Original Process.—Twenty-seven grammes of the oil are dissolved in 50 c.c. of normal petrol, 30 c.c. of concentrated sulphuric acid are added without stirring, then while cooling add 15 c.c. of 40 per cent. formaldehyde, shake until no more heat is given off, cooling between shaking, let stand for half an hour, then pour into 300 c.c. of water, and wash the flask out with water; the acid solution is next saturated with ammonia, the precipitate is sucked off and washed with petrol to remove free oil, and then with water until the washings are acid free. The precipitate is dried at 105° C. to constant weight.

The process was tried with a view of having another method for determining the origin of a given sample; when a sufficient quantity of the sample is available there is no difficulty in doing this, but, unfortunately, there are many cases when one has only 25–30 c.c. of a sample for the whole examination, so experiments were made in the direction of cutting down the amount of oil used for the test. During these experiments it was found that the reaction was not complete during the few minutes of shaking and cooling, and also that doubling the amount of formaldehyde, with the object of increasing the speed of the reaction, gave a large increase in the amount of precipitate; if the acid doubled as well, the amount of precipitate is only the same as the original process.

The process is now carried out as follows:—Weigh out 2 grammes of the sample into a 300 c.c. flask, dissolve in 50 c.c. of petrol 0·64 specific gravity, 3 c.c. of concentrated sulphuric acid, and 6 c.c. of 40 per cent. formaldehyde added without shaking, then cool under the tap and shake until cold; the shaking is then continued for fifteen minutes longer, next add 50 c.c. of water, shake, and add excess of ammonia. The precipitate is now filtered off through a dried and weighed filter, the filter washed first with petrol to remove free oil, and then with water until free from ammonia and sulphates. The precipitate is then dried in the water oven to constant weight.

OIL.	FORMOLITE PRECIPITATE.	OIL.	FORMOLITE PRECIPITATE.
	Per cent.		Per cent.
American 885/890	46·31	American mineral colza	20·97
Scotch 885/890	31·39	American 865 neutral	9·27
Galician 885	74·86	,, 45 cold test filtered cylinder.	6·43
Russian 895	47·10		
,, 907	30·50	Texas 930 red oil	19·42
Galician 907	34·95	Pennsylvania 912/915 red oil	21·00
Pennsylvania 900/907	31·86	Russian 890 half-white oil	8·10
Texas 925	32·88	American 860 half-white oil	7·45

The following give the iodine value of a few mineral oils, the oils from different sources being placed in order of rising iodine values :—

OIL.	IODINE VALUE.	FORMOLITE VALUE.
	Per cent.	Per cent.
Russian 895	3·0	47·1
,, 907	6·0	30·5
,, 890 half-white	9·0	8·10
Galician 907	6·1	34·95
,, 885	10·4	74·86
American 860 half-white	7·3	7·45
,, mineral colza	8	20·97
,, 915 red	8·9	19·42
,, 900/907 pale	10	31·86
,, 860/865 pale neutral	11·2	9·27
,, filtered valve	13·3	6·43
,, 910/915 red	15·3	21·0
,, 885 pale spindle	18·3	46·3
Scotch 885	21	31·2

Testing the Refining of Mineral Oils.—According to the authorities, an oil which has been insufficiently treated with acid will, on shaking with its own volume of sulphuric acid—specific gravity varying according to different authors from 1·53 to 1·75 hot, cold, or both—turns the acid brown. On trying this it was found that no commercial oil turned acid of 1·53 specific gravity brown, even cold. The general order in which the acid refining stands according to this test is :—

1. Thompson and Bedford American oils.
2. Better Scotch oils.
3. Russian mineral oils.

Level with the Russian oils are Galician, Texas, and Pennsylvanian oils of other makes.

This test is evidently too severe for present-day refining. When using a mixture of 1 part of concentrated sulphuric acid and 1 part of water by volume, and mixing equal volumes of acid and oil, the first three classes given above show no change when cold, and on heating the mixture to 212° F. the acid is only slightly coloured, and the oil is paler than the original sample, but even this test does not pass many oils now marketed in large quantities.

The Soda Treatment.—Equal volumes of the oil and caustic soda solution (33 per cent.) are shaken together and put in the hot water oven to separate. If the soda solution separates slowly and is milky, it shows that the oil was not sufficiently treated with soda during the refining. This fault appears to occur more often with Scotch oils than any other, because the Scotch oils contain a fair quantity of phenoloid bodies, and increased soda treatment means increased loss to the producer, both in cost of refining and of course a smaller yield of finished oil.

Washing after Treatment.—Equal volumes of the oil and hot water are shaken together and put in the hot water oven to separate. If the oil has been properly washed the oil and water will separate quite clear, but if not properly washed the water will separate more or less turbid. As previously mentioned, the heavy Texas oils are the greatest sinners in this respect, but all oils which have been blown instead of washed turn the water turbid.

Combined Sulphuric Acid in Mineral Oils.—All mineral oils contain more or less aromatic compounds, and these are liable to sulphonation during the refining, and so are often to be found in the finished oils. On heating the oil with its own volume of newly distilled aniline the presence of sulphonic acids is shown by the mixture becoming more or less turbid owing to separation of aniline sulphate.

Metallic Soaps in Mineral Oils.—The addition of oleates of lead, alumina, or calcium to mineral oils is not as frequent as was formerly the case. This addition raises the specific gravity but little, so that an oil having a very high viscosity for a given specific gravity is sure to contain either metallic soaps or indiarubber. If the suspected oil be boiled with hydrochloric acid for thirty minutes, adding water to make up for the evaporation, the acid liquor rún off and tested in the usual way for bases, then, after washing the oil until acid free, the viscosity of the oil is taken from a 10 c.c. pipette, and if metallic soaps have been added to the sample its viscosity will be found to be very much lower than that of the original sample.

Indiarubber in Mineral Oils is detected by boiling the oil with a mixture of 3 parts of ether and 4 parts of alcohol, which will precipitate the indiarubber present; the precipitate if desired may be filtered off, washed, dried, and weighed.

Dark Cylinder Oils may be divided into two classes: (1) with asphaltum below 0·5 per cent., (2) with asphaltum over 0·5 per cent.

The two classes can be separated by mere inspection of the bottles in which they are contained. The oils with low asphaltum content will leave a perfectly smooth coat of oil on the bottle side, which will remain smooth as long as it stays on the glass. The oil with high asphaltum content will leave in the layer on the bottle side many finely divided particles, which are left on the glass as the oil gradually flows away from them.

Asphaltum in Dark Cylinder Oils.—Dissolve 2 grammes of the oil in petrol of 0·64 specific gravity, allow to stand three hours, filter off, and wash the filter with petrol until fat free. The residue on the filter is dissolved off into a weighed flask with hot benzol, the benzol distilled off, and the residue dried and weighed.

The amount of asphaltum in dark cylinder oils is very variable, ranging from 0·03 per cent. to 2·25 per cent., these being the limits found in about 100 estimations.

If a dark cylinder oil contains much over 1 per cent. it will turn quite solid after twelve hours' heating at 212° F., which shows what will happen to the oil in a steam cylinder where it may be exposed to a much higher temperature than 212° F. The highest percentage of asphaltum found in black mineral oils, fuel oils, etc., was 2·18 per cent.

Oil.	Percentage of Asphaltum.
Medium dark machinery	0·03
American black oils	1·02
,, dark cylinder oils	0·07 to 2·25
Russian residuum	0·34

A sample of dark cylinder oil had specific gravity ·9308, and contained 1·59 per cent. of asphaltum, determined as above. After removing the asphaltum the specific gravity of the oil was only ·9083.

Connection between Analytical Results and Practice.—Looking at the question from a theoretical point of view, if one leaves out oils with a very low viscosity, there is no doubt a close connection between the Redwood figures and the internal friction of the oil; from this a first-class oil should have as high a viscosity as can be obtained for a given specific gravity.

The lower the iodine value the higher the viscosity, and also the less liability for oxidation to take place during use.

The less the interval between the vapour point and the flash of the oil the less wasteful the oil will be in use, always provided that the bearings on which the oil is used are kept in good condition.

The cold test like the specific gravity should be the lowest obtainable for a given viscosity.

The oil should have a vapourising point 150° F. above the temperature at which it has to be used.

The flash point will but rarely come into consideration, as there are no lubricating oils on the market with a flash point below 300° F., which is quite high enough for safety, in spite of the insurance limit of 340° F. The following offers comparison of these requirements with actual figures obtained from good oils of their class now on the market:—

MINERAL OILS (AVERAGE FIGURES).

OIL.	SPECIFIC GRAVITY.	REFRACTIVE INDEX AT $\frac{60}{60}$ ° F.	IODINE VALUE AT 70° F.	VISCOSITY AT				VAPOUR ° F.	OPEN FLASH ° F.	COLD TEST ° F.
				70° F.	140° F.	180° F.	212° F.			
American Crude Oils— Texas Crude	·9343–·9425	...	13·1	...	110–137	61	...	160–170	235–292	23–31
American Black Oils— Fuel Oils (Texas)	·9411–·9430	...	...	...	290	...	...	...	195–275	30–32
Grease Oils	·9463–·9513	...	...	...	345–362	142	...	...	173–240	32–36
Residuum Oils (Texas)	·9444–·9458	...	...	...	160–206	75–90	...	...	312–360	23–39
Summer Dark	·8890–·8923	...	...	...	260	120–128	72–93	...	437–440	71–76
Winter ,,	·9164	...	19·3	...	180	78	...	...	398	25
Medium ,,	·8808	...	...	973	122	68	48	...	406	32
American Refined— Mineral Colza	·8225–·8252	1·4576–1·4586	8·0	42–48	...	...	...	...	248–262	
Sun-Bleached Neutral	·8411	1·4646	...	50	...	...	...	118	262	
Penna 850 ,,	·8513	...	...	104	44	...	...	148	320	18
,, 865	·8678	...	...	57	...	...	...	...	266	23
,, ,, Neutral	·8632–·8716	1·4813–1·4871	11·2	253–271	57–62	...	...	220–230	369–400	20–23
,, 875	·8740–·8775	1·4919	...	70–108	35	...	...	145–192	275–300	18–22
,, 885	·8853–·8947	1·4967–1·5021	18·3	131–191	43–49	...	...	160–208	332–343	21–25

MINERAL OILS (AVERAGE FIGURES)—*continued.*

Oil.	Specific Gravity.	Refractive Index at $\frac{60}{60}$ ° F.	Iodine Value at 70° F.	Viscosity at				Vapour ° F.	Open Flash ° F.	Cold Test ° F.
				70° F.	140° F.	180° F.	212° F.			
American Refined—										
,, 895	·8961–·9008	1·4957–1·5051	6·7	275–306	59–61	...	...	200–208	359–386	20–25
,, 900/7	·8993–·9050	1·5051–1·5061	9·7–10·5	348–390	66–70	44	37	200–215	374–390	22–25
,, 905	·9038–·9107	1·5033–1·5235	11·1	479–534	7 8	60	40	210–235	375–411	24–26
,, 912/15	·9105–·9149	1·5107–1·5134	7·9	677–764	95–102	54	43	230–241	390–425	23–25
,, Red 912/15	·9072–·9160	1·5152	15·3	614–674	91–103	51 55	40–43	225–240	389–409	25–26
American Half-White—										
845/50	·8486	1·4715	9·1	125	47					
855/60	·8578	1·4739–1·4754	0·7–9·0	136–239						
American Red (Kansas)	·9201	...	...	811	122	...	...	232	415	27
Queen's Heavy ,, ,,	·9167–·9223	...	...	1132–1224	136–148	70	50	235–268	410–442	26–28
No. 2 ,, ,,	·9126	...	...	480	78	...	...	233	385	25
Texas 920/5 Pale	·9176–·9318	...	9·2	312–375	55–68	...	...	150–200	300–335	16–23
,, 930/5 Red	·9300–·9386	...	12·4	883–1770	94–137	...	...	171–200	340–350	24–26
,, 940/5 ,,	·9433–·9524	...	12·9	3300–5563	192–268	81–98	55–57	200–270	375–412	24–27

American Filt. Cylinder—Low Cold Test, FFF	·8893–·8916	...	13·3	...	532–575	213–232	119–139	320–340	525–547	42–46
,, ,, ,, CT	·8884–·8894	...	8·8	...	371–424	162–205	96–102	310–325	489–493	44–49
High ,, ,, Cosmos	·8876–·8892	...	10·3	...	318–338	138–148	80–92	280–295	470–490	78–84
,, ,, ,, EFC	·8880–·8901	...	6·9	...	402–465	184–200	105–114	310–325	520–533	70–76
American Dark Cylinder—Anglo Loco	·9013–·9024	...	11·7–13·1	...	...	300–320	146–163	340–360	560–597	49–52
W ,, ,,	·9020–·9158	...	17·7	...	...	350–395	174–198	320–335	564–588	49–52
Anglo A ,, ,,	·8980–·9015	...	11·8	...	...	203–210	110–112	270–290	500–527	48–52
,, N ,, ,,	·8894–·9018	...	11·3	...	...	245–254	130–140	300–330	530–550	44–47
Galician Oils—880/885	·8803–·8910	...	13·2	100–177	40–45	...	...	165–180	300–337	27–38
900/905	·9026–·9064	...	...	318–348	60–66	...	...	190–210	350–365	28–31
912/916	·9157–·9179	...	8·9	1048–1158	119–130	64	47	215–236	390–405	25–28
Black Axle Oil	·9422	...	...	1080	118	...	...	185	378	36
Roumanian—Residuum	·9450–·9465	...	17·8	3970	234–310	100	...	172–180	310–316	27–40
Russian Oils—White Oils	·866–·876	1·4774–1·4862	...	132–234						
Half-White Oils	·878–·896	1·4710–1·4831	...	188–704	56–82	...	...	178–228	318–380	

MINERAL OILS (AVERAGE FIGURES)—*continued.*

OIL.	SPECIFIC GRAVITY.	REFRACTIVE INDEX AT $\frac{60}{60}$ ° F.	IODINE VALUE AT 70° F.	VISCOSITY AT				VAPOUR ° F.	OPEN FLASH ° F.	COLD TEST ° F.
				70° F.	140° F.	180° F.	212° F.			
Russian Oils—										
895 Spindle	·895–·901	1·4929–1·4963	2·6–3·0	330–487	61–81	...	...	184–225	330–362	15–31
907 Engine	·905–·910	1·4986 1·5061	3–8·5	974–1380	112–147	60–64	46–48	196–246	364–406	14–26
912/15 Cylinder	·907–·917	...	10	...	195–1074	83–350	53–167	218–355	400–515	24–29
Residuum	·908–·915	...	6·9	1750–1860	176–201	80–93	61	170–212	316–341	22–33
Scotch Oils—										
860/8	·8647–·8748	1·4852 1·4933	28·8–41·6	58–73	35	...	...	130–202	267–320	21–26
875	·874–·875	...	...	70–93	38	...	...	158–166	295–298	22
885	·883–·895	1·5023–1·5061	20·2–22·2	107–184	42–53	...	...	164–238	320–360	17–28
895	·893–·907	...	...	181–239	47–60	...	...	170–232	326–371	15–23

PETROL JELLY.

Two varieties are to be found, the natural jellies and the artificial. The latter may be anything from mixtures containing 75 per cent. natural jelly to a mixture of ceresin or paraffin wax and a light mineral oil.

Specific gravity: natural jelly, ·860 to ·890, according to the melting point; the higher the melting point, the higher the specific gravity.

Similar limits are found for the artificial jelly, except in the case of very poor imitations, when the specific gravity may rise to ·900.

Melting point varies in both kinds from 95 to 115° F., the cold test from 90 to 100° F.

Refractive index is higher in natural jellies (over 1·485) than artificial (1·472 to 1·477) at 140° F.

Viscosity: this gives the most certain indication as to purity.

NATURAL JELLY.

Viscosity 142 Redwood at 140° F., cold test 95° F.
,, 135 ,, ,, ,, ,, 94° F.
,, 320 ,, ,, ,, ,, 117° F.
,, 379 ,, ,, ,, ,, 114° F., this sample was almost as dark in colour as a filtered cylinder oil.

ARTIFICIAL JELLY.

Viscosity 58 at 140° F., mixture of wax and mineral oil.
,, 65 ,, ,, ,, ,, ,,
,, 70 ,, ,, ,, ,, ,,
,, 108 ,, ,, ,, ,, ,,
,, 185 ,, ,, ,, ,, ,, and natural jelly.

The last sample was made specially in order to see whether it was possible to make an artificial sample having a viscosity as high as the natural jelly.

Coke is higher in the natural than in the artificial:—

Natural Jelly—5 to 6 per cent. for 100° F. cold test.
,, ,, 7·5 per cent. for 117° F. cold test, colour pale.
,, ,, 11·13 per cent. for 110° F. cold test ,, dark.

Artificial jelly is always below 5 per cent., even in samples containing a high percentage of natural jelly.

The reason for this is that the coke in ceresin, paraffin wax, and light mineral oil is always low:—

White Ceresin, 1·1 per cent.; Light Oils, 1·1 to 3·3 per cent.

The tenacity of petrol jellies varies with the viscosity of the sample at 140° F. The lower the viscosity, the lower the tenacity.

Detection of Ceresin.—Dissolve 1 gramme of jelly in 10 c.c. of carbon disulphide, and keep the solution at a temperature of 70° F.; if ceresin is present the solution will either turn turbid or show a flocculent layer on the top, according to the amount of ceresin present. The above does not give any precipitate or turbidity with paraffin wax.

Paraffin Wax in Petrol Jelly.—Before testing for paraffin wax, the absence of ceresin must be proved as above.

Dissolve the sample in alcohol-free ether, and when cool add the same volume of absolute alcohol; a bulky white precipitate will form at once if paraffin wax is present; filter off, and wash with alcohol-ether (1 to 1), and take the melting point of the separated wax. It must be remembered that this is only a qualitative test, and further, that the melting point of the precipitated wax will be higher than that of the wax used, because the paraffin wax is a mixture of bodies of different melting point, and the fractions of highest M.P. are precipitated first.

Saponifiable Matter in Petrol Jelly.—The acidity of petrol jelly should always be determined, because this will at once detect the use of so-called ceresin samples which contain resin or shellac; but in some cases castor or other oils have been added to petrol jelly, and of course the saponifiable can only be determined by saponificate separation and weighing the separated saponifiable matter.

Samples of petrol jelly containing saponifiable matter turn rancid, and also will not pass the B.P. tests.

Iodine Value.—This is not of much value, because a genuine white jelly like a white oil has most of its unsaturated constituents removed during preparation, and has practically no iodine value. In the case of the yellow jelly, since the highest iodine value one finds in a filtered cylinder oil is 15, this figure gives us an upper limit for iodine value. For artificial jelly, since the paraffin scale used has but little iodine value, and the light oils used do not exceed an iodine value of 12, here again we obtain a fairly good upper limit. In actual practice the highest iodine value for a white jelly was 6, and for yellow jelly 11·3.

PARAFFIN WAX.

The usual commercial grades are yellow, semi-refined, and refined.

Melting point varies from 102 to 150° F.
Specific gravity ,, ·8410 to ·8860 at 60° F.
Iodine value ,, 1 to 10·5.

The specific gravity if taken on samples of different melting point but from the same source rises with the melting point.

The degree to which the refining has been carried may be told by heating the sample in a test-tube with concentrated sulphuric acid; the colour of the layer of wax is darker or paler according to the extent to which the refining has been carried.

Source.	Specific Gravity.	Iodine Value.
Scotch 110/112 M.P.	·8828	10·5
,, 118/120 ,,	·8812	4·9
,, 120/127 ,,	·8855	3·3
American 106/108 ,,	·8533	5·4
,, 120/122 ,,	·8410 to ·8636	1·9
,, 135/140 ,,	·8590 to ·8772	1·0
,, 130 M.P. yellow	·8823	3·5

CERESIN AND ITS IMITATIONS.

Ceresin itself is very rarely found on the market; the usual commercial article is a mixture of ceresin and paraffin, but resin and other bodies are also used. The difference between melting point and cold test in the case of pure ceresin is usually about 4° F., but in mixtures of ceresin and paraffin—that is, most of the commercial ceresins with melting point from 140 to 160° F.—the difference between melting point and cold test is sometimes as much as 10 to 12° F.

The specific gravity should always be taken, because the specific gravity of ceresin is over ·910, and commercial paraffin is always under ·900. The acidity also should never be omitted; in natural ceresin and paraffin wax the acidity as oleic acid is below 1·5 per cent., but if resin or shellac has been added the acidity rises with the percentage added. Commercial yellow ceresins, with the exception of the grade known as natural yellow, are coloured with coal-tar dyes, which may be removed by boiling out the sample with alcohol. The class of dye most often used seems to be the Soudans, made by the Berlin Aniline Co. Although these colours do not give any characteristic absorption bands with the spectroscope, they are easily identified.

Soudan 1 gives a red colouration with conc. sulphuric acid.
,, 2 ,, ,, ,, ,, ,, ,, ,, stronger than 1.
,, 3 ,, a dirty brownish-green with concentrated sulphuric acid.
,, 4 ,, a full bright green ,, ,, ,, ,,

Quinoline yellow is used for lemon yellow.

Resin in Ceresin.—Qualitative detection by the Liebermann-Storch reaction may be determined quantitatively by either volumetric or gravimetric method.

Volumetric Analysis.—Dissolve 5 grammes of sample in petrol, add an equal volume of neutralised alcohol, and titrate with N/10 alkali, basing the calculation on the average acidity of resin being 85 per cent. as oleic acid. The acidity in ceresin is so low that it may be neglected in the calculation.

Gravimetric Analysis.—Saponify 5 grammes of sample with alcoholic potash, and shake out with petrol as usual. Decompose the soap solution with acid, and shake out the resin with ether, wash, distil the ether off, dry, and weigh. The results, like all other resin estimations, are always high, so that the volumetric method is practically as accurate, and much quicker.

Estimation of Paraffin in Ceresin and Ozokerite.—A method depending on the following experiments has been worked out by Marcusson and Schluter:—

1. A solution of ceresin in carbon disulphide has from 55 to 66 per cent. of its hydrocarbons precipitated by the addition of a mixture of alcohol and ether under certain conditions, whilst paraffin of every kind remains entirely in solution.

2. A mixed solution of paraffin and ceresin under the same conditions has part of its hydrocarbons precipitated by alcohol-ether; the amount of precipitate is always about 60 per cent. of the ceresin contained in the mixture.

Three grammes of the sample, after carefully freeing the sample from any resins, fats, or weighting materials it may contain, are dissolved in 30 c.c. of carbon disulphide by gentle warming under reflux, the solution is brought to 77° F. in a water bath (the more ceresin present in the sample the greater the turbidity of the solution at this stage); 300 c.c. of alcohol-ether (1 to 1), the alcohol of 96 per cent. at 77° F. are added, and the precipitate quickly sucked off through a Buchner funnel; the precipitate is washed with 25 c.c. of the alcohol-ether mixture (at 77° F.), and the precipitate then dissolved into a weighed flask with benzol, the benzol distilled off, and the residue dried and weighed. The percentage of paraffin is calculated from the weight of the precipitate as follows:—

Whilst 60 per cent. of precipitate corresponds to 100 per cent. ceresin,

$$a \text{ per cent. of precipitate} = \frac{100a}{60} \text{ per cent. ceresin.}$$

When p = percentage of paraffin,

$$p = 100 - \frac{100a}{60} = \frac{5}{3}(60 - a).$$

Shellac in supposed ceresin. The sample was offered as white ceresin.

Specific Gravity	·9207	Melting Point	191° F.
Acidity	5·29% as oleic acid	Cold Test	184° F.

Five grammes of the sample were saponified with alcoholic potash, the solution allowed to cool, and poured into a separator, leaving the cake of wax behind in the flask. The cake was again boiled up with alcoholic potash, and the potash solution again poured into the separator, still leaving the cake in the flask; the cake was washed with water, and its melting point determined. The figure found was 140° F.

Neither the original sample nor the separated saponifiable from it gave the Liebermann-Storch resin reaction. The saponifiable was found to be from white shellac.

Quite a number of similar samples have been examined since, usually having melting point 190 to 192° F., and acidity 5 to 7 per cent. as oleic acid.

Sample.	Specific Gravity.	Acidity.	Melting Point.	Cold Test.
White	·8560	0·35–1·06	137–141° F.	125–135° F.
Yellow	·9006	0·98	140 ,,	133 ,,
,,	·9132	0·70	141 ,,	126 ,,
,,	·8971	0·98	138 ,,	125 ,,
Black	...	1·06	...	140 ,,

RESIN OILS.

Specific Gravity	·9709 to 1·0148	Iodine Value	52·9 to 84·2
Acidity as oleic	nil to 41·60 per cent.	Refractive Index	1·5133 to 1·5428

For the preparation of emulsion oils a resin oil with an acidity below 15 per cent. is not much good.

RESIN OIL GREASES (SET GREASES).

Water and loss	15 to 30%	Resin oil and mineral	35 to 50% (largely mineral)
Lime	15 to 35%		

LUBRICATING GREASES.

These are of two kinds: cup greases, made usually from liquid oils saponified with lime; and engine greases, made from oil mixtures containing some solid fat and saponified with soda.

These greases also vary greatly as regards filling material, although the fillers are supposed by the makers to add to the lubricating value of the product.

Water is determined in the water oven or, better, by distillation.

Fat and Bases.—Five grammes of the sample are weighed into a flask and boiled up with hydrochloric acid until the fatty layer is quite clear; the addition of a piece of porcelain will do away with bumping, which might otherwise spoil the test. When the fat is clear, the flask and contents are cooled under the tap, and shaken out twice with ether, the ether extracts washed with water until acid free, the ether distilled off, and the residual oil dried in the oven, cooled, and weighed. The oil is put on one side for further examination. The acid solution and washings are mixed together and examined for bases.

Free Acid is determined in the same way as in oils and fats.

Free Alkali, like free acid, is sometimes found in badly prepared greases, and is easily detected with phenolphthalein; the determination of the amount present is made by dissolving up as for free acid, but the titration is carried out with N/10 acid, and the result calculated to the base present.

There is no connection between the dropping point and the percentage of water in these greases.

Total Fat	95·14	94·14	90·74	72·51
Water	3·96	4·54	6·51	18·27
Soda	2·50	2·19	2·70 CaO	8·10 CaO
Fat contains—				
Saponifiable . . .	23·25	23·35	17	
Unsaponifiable . . .	76·22	76·40	83	

APPENDIX.

OILS, FATS, AND WAXES OF THE BRITISH PHARMACOPŒIA.

The following are the limits allowed in the tests of these samples:—

Acidum Oleicum (Oleic Acid).—Specific gravity ·890 to ·910. Cold test 40° to 41° F. Dissolve 1 gramme in 15–20 c.c. 90 per cent. alcohol, add phenolphthalein and aqueous 25 per cent. caustic, drop by drop, until pink, make just acid with acetic acid, and filter. Mix 10 c.c. of the filtrate with 10 c.c. ether and 10 c.c. aqueous lead acetate solution; only a slight turbidity should result.

Adeps (Lard).—Saponifiable value 192 to 197. Iodine value 52 to 63. Acidity 0·3 per cent. max. Refractive index 1·453 to 1·455. Melting point 38 to 41° C.

Adeps Lanæ (Anhydrous Lanolin).—Melting point about 40° C. Ash not above 0·3 per cent.

Cera Alba (White Beeswax).—Five grammes must take 1·5 to 2·2 c.c. N/1 alkali to neutralise the free fatty acids, and 6·2 to 6·8 c.c. N/1 alkali for saponifiable.

Cetaceum (Spermaceti).—Specific gravity ·94 to ·95. Melting point 42 to 50° C. Iodine value 3 to 4·4. Saponifiable value 125 to 136.

Oleum Amygdalæ (Almond Oil).—Saponifiable value 188 to 200. Iodine value 95 to 100. Specific gravity ·915 to ·920. Free fatty acids up to 2 per cent. Refractive index 1·472 to 1·473. Setting point − 18° C. Biber's test to be used to detect other kernel oils.

Oleum Lini (Linseed Oil).—Saponifiable value 187 to 195. Iodine value 170 to 190. Specific gravity ·930 to ·940. Acidity up to 1·5 per cent. Refractive index 1·4835. Setting point not below − 20° C. Unsaponifiable matter under 1 per cent. Sulphuric acid and acetic anhydride test to detect resin oil.

Oleum Morrhuæ (Cod Liver Oil).—Saponifiable value 179 to 198. Iodine value 155 to 173. Specific gravity ·920 to ·930. Acidity under 1 per cent. Refractive index 1·4800 to 1·4830. Unsaponifiable not over 1·5 per cent. After 10 hours at 0° C. must not separate solid particles.

Oleum Olivæ (Olive Oil).—Saponifiable value 188 to 197. Iodine value 79 to 87. Specific gravity ·915 to ·918. Acidity up to 3·5 per cent. Refractive index 1·4698 to 1·4713. Halphen's test for cotton oil. Baudoin's test for sesame oil. Nitric acid for cotton oil, and the following test for the qualitative detection of arachis oil:—A mixture of 1 c.c. oil and 15 c.c. alcoholic N/1 potash is boiled under reflux for fifteen minutes, then kept at a temperature not exceeding 15° C. for twenty-four hours; must not become cloudy, nor separate crystals of arachidate.

Oleum Ricini (Castor Oil).—Saponifiable value 177 to 187. Iodine value 83 to 89. Specific gravity ·960 to ·970. Acidity up to 2 per cent. Refractive index 1·4790 to 1·4805. The oil is soluble in absolute alcohol in all proportions, soluble in glacial acetic acid, and also in 3·5 volumes of 90 per cent. alcohol. Ten c.c of oil shaken in a glass-stoppered cylinder with 7 c.c. petrol-ether dissolves clear at 15° C.; a further 3 c.c. of petrol causes turbidity, but after five minutes at 21° C. clears again, the turbidity reappearing at 18° C.

Oleum Theobromatum (Cocoa Butter). — Specific gravity ·990 to ·998. Saponifiable value 188 to 195. Iodine value 35·5 to 37·5. Melting point 30 to 33° C. One gramme dissolved in ether (3 c.c.) at 17° C. and cooled to 0° C. must not separate solid in three minutes. On again warming to 15·5° C. the mixture must gradually clear. The melting point must not be taken until the sample has stood forty-eight hours after preparing. Acidity not over 1 per cent.

Paraffinum Durum (Paraffin Wax).—Specific gravity ·82 to ·94. Melting point 54 to 60° C. No ash. The alcoholic extract must not turn blue litmus paper red.

Paraffinum Liquidum (White Mineral Oil).—Specific gravity ·860 to ·885. Four c.c. oil, 2 c.c. absolute alcohol, and 2 drops of a saturated solution of litharge in caustic soda must remain colourless after heating to 70° C. for ten minutes (absence of sulphur compounds). Ten c.c. of alcohol boiled with 5 c.c. oil must not redden blue litmus paper.

Paraffinum Molle (Petrol Jelly).—Specific gravity at melting point ·840 to ·870. Melting point 36 to 42° C. Ten c.c. alcohol boiled with 5 grammes must not redden blue litmus paper. Ten grammes boiled ten minutes with 20 c.c. of caustic soda solution, the soda solution separated and acidified with sulphuric acid, must give no precipitate or separate oily bodies. Absence of fatty oils, fats, and resins. No ash.

Sevum Præparatum (Prepared Tallow).—Saponifiable value 192 to 195. Iodine value 33 to 46. Melting point 45 to 50° C. Refractive index at 60° C. 1·4491 to 1·551. Acidity not above 1 per cent.

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