PERFUMES AND COSMETICS

PART I

RAW MATERIALS

CHAPTER I

* NATURAL, RAW MATERIALS USED IN PERFUMERY

Water

Although water is very little used in the manufacture of perfumes, properly so called, it plays a considerable part in the dilution of the alcohol used in the preparation of perfumes which have very little alcohol in them, and in toilet soap base. Therefore it will not be waste of time to devote a few lines to this substance. There is no need to examine its physical and chemical properties, they are well enough known by all, and we will commence at once with the most important point, viz., the purity of water.

Water in its natural state is never pure. It always contain, in more or less considerable quantities, gases, and organic and mineral matters, either suspended, dissolved, or chemically combined. Thus in a manufacture such as we are dealing with, water containing suspended impurities should be purified by allowing the impurities to settle, or by decantation and filtration. Those which contain impurities which are dissolved or chemically combined are generally divided into soft waters and hard waters, or waters containing much chalk or sulphate of lime; and into pure waters and impure waters, according to the amount of organic matter dissolved in them. Nothing but pure soft water, or, better still, water that has been purified by distillation and filtration, should be used in the manufacture of actual perfumes. Rain-water and water condensed by steam-generators, which is
similar to distilled water, are not pure enough, and often cause trouble in the manufacturing process which is at first inexplicable, but which proves on investigation to be caused by impurities in the water.

Filtration of Water.—Whenever the water comes from—whether it be river, spring, or rain-water— it should always be filtered. This is more necessary in the manufacture of perfumery than in any other industry.

It often happens, especially in small towns, that well-water is contaminated by infiltrations of sewage material. Chemical analysis of this type of water shows a high percentage of organic matter, nitrates and ammonia. From this it may also be concluded that objectionable micro-organisms are to be found in the water, and it should never, in any circumstance, be used for perfume manufacturing purposes.

Distillation of Water.—It is often incorrectly stated that good spring water, or water that has been boiled, can be used instead of distilled water for the preparation of dilute alcohol.

Thus, certain essential oils dissolved in alcohol will bear the addition of a much larger quantity of distilled water without becoming turbid, than of ordinary or boiled water. The turbidity is generally brought about by the precipitation of the mineral salts in a colloidal form and necessitates a very careful filtration. It is especially easy to prove this when using oils free from terpene, which, when used in alcohol diluted with distilled water within reasonable limits, generally give no turbidity.

The distillation of water is very simple, but unless certain precautions are taken, the water will be little better for the distillation. To get the distilled water clear and clean for diluting purposes, the still must be perfectly clean and free from verdigris. Further, the water to be distilled must also be pure and freed from suspended matter by filtration. The still should only be filled to three-quarters of its capacity, so as to ensure that only steam enters the condenser. The distillation must proceed slowly over a gentle fire. The first portion of the distillate, slightly contaminated with metal, is rejected. About 75 per cent. of the contents of the still are now condensed, leaving the remainder, in which are to be found the accumulated impurities, in the still. This residue is then run off. The water distilled in the middle of the operation, if the still has been properly constructed, is of extreme purity, but is subject to deterioration. To preserve its purity, it is advisable to add 10 per cent. of alcohol. Unless
this is done, the cost of distillation is wasted. Carefully distilled water is excellent for the purpose of reducing alcohol. It is clear, tasteless, and without odour.

Water taken from steam engines must never, on any account, be used, as it always contains traces of oil which are very difficult to get rid of. This oil is rancid, and often contains fatty acids, which give an undesirable taste and odour to the water, and render it unfilterable.

Fig. 1—Still for distillation of water.

Deroys still (Fig. 1) is specially constructed for the distillation of water. It works in an admirable manner, much to the satisfaction of those using it, who are able to obtain from it water which is chemically pure. It has a constant and automatic feed.

ALCOHOL

Properly speaking, this word is the common name for a special kind of alcohol—the oldest kind known, viz., ethyl alcohol. The early Arabian doctors extracted it from wine, and employed it as a medicine. To-day it is one of the most important industrial products, and thousands are employed in its
manufacture. The perfumery industry employs it largely, and for that reason it will be necessary to deal specially with it in these pages, as well as because of its many other uses and its financial importance. Ethyl alcohol, used more especially in the manufacture of essences, is not a product of nature except to a minute extent, but results from the fermentation of sacchariné matters. The fermentation requires:—

1. Sugar, or a carbohydrate yielding sugar.
2. Eight times as much water as the sugar to be converted.
3. Atmospheric air, or a generator of oxygen.
4. Enough yeast to transform the sugar into alcohol.
5. A temperature of 20° to 30°.

The raw materials which furnish the sugar are of very different characters, and are derived either from fruits, such as the grape, apple, and pear, from the conversion of starchy matters, such as rice, maize and other cereals, menioe and potatoes, or from the juice of the sugar-beet or the sugar-cane. The ethyl alcohol as manufactured in distilleries corresponds to the chemical formula (C₂H₅O). In a pure state, and completely free from water (absolute alcohol), it is a colourless liquid, very mobile and inflammable, of an agreeable and invigorating odour, and a burning taste. Its specific gravity is: 0·8095 at 0°; 0·7987 at 5°; 0·7939 at 15°; and 0·792 at 20°. Its boiling point is 78·5°; when subjected to intense cold (—100°), the liquid becomes thick, but so far it has not yet been solidified. Commercial ethyl alcohol nearly always contains either aldehyde or other alcohols dissolved in it. These impurities are eliminated by rectification. In France, many of the distilleries refine their own alcohols, but in other countries it constitutes a special industry. The impurities which contaminate crude alcohol are classed under the generic name of Fusel Oil. These impurities are composed of a series of bodies which are formed during the fermentation as secondary products, and give a disagreeable taste to the alcohol. Little is known of their origin, which is attributed by Brefeld to the residual products of the yeast organisms; the author, on the contrary, thinks that certain of the raw materials employed have something to do with their formation.

It is certain, however, that the alcohols derived from cereals, potatoes, molasses, and sugar-beet are of a different nature from those of brandy from wine and fruits. To the first category the

* Unless otherwise indicated, all temperatures are in degrees Centigrade.
NATURAL RAW MATERIALS USED

fusel oil gives a repugnant taste and smell, to the second an agreeable odour, so long as it is not present in too great quantity. The dominant bodies in the fusel oil of potatoes are the amylic, propylic, and isopropylic, butylic, and isobutyllic alcohols. In that from cereals, oenanthic ether and amyl alcohol. In molasses they consist principally of caproic, caprylic, and capric esters.

Acetic acid is found in all kinds of fermenting liquors, produced by the oxidation of the alcohol. From this acid originates ethyl acetate and numerous compound esters. Thus one finds aldehyde, and also other bodies which greatly resemble it, metaldehyde, erotoic aldehyde, and aetet. It is not yet known whether the three latter are originally contained in fermenting liquors or whether they are produced from a secondly action during the process of distillation. The impurities contained in crude alcohol may be divided into three groups.

1. Very volatile products

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>22°</td>
</tr>
</tbody>
</table>

2. Less volatile products, soluble in dilute alcohol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Alcohol</td>
<td>78°</td>
</tr>
<tr>
<td>Propyl Alcohol</td>
<td>85°</td>
</tr>
<tr>
<td>isoPropyl Alcohol</td>
<td>97°</td>
</tr>
<tr>
<td>Butyl Alcohol</td>
<td>108-5°</td>
</tr>
<tr>
<td>isoButyl Alcohol</td>
<td>117°</td>
</tr>
</tbody>
</table>

3. Slightly volatile products, insoluble in dilute alcohol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amyl Alcohol</td>
<td>130°</td>
</tr>
<tr>
<td>Ethyl Caproate</td>
<td>165°</td>
</tr>
<tr>
<td>Ethyl Caprylate</td>
<td>208°</td>
</tr>
<tr>
<td>Ethyl Caprate</td>
<td>244°</td>
</tr>
</tbody>
</table>

In distilling, the properties of these different impurities are taken into account to remove them from the crude alcohol. For this purpose, the latter is diluted to 50 per cent. strength, when the insoluble bodies, or those difficult of solution in dilute alcohol, are thrown out of solution, and can be eliminated by filtration. If afterwards the filtered crude alcohol is distilled, the aldehyde, which is very volatile, is found in the first runnings. Ethyl alcohol then comes over in an almost pure state of 95—96% strength.

Finally, dilute alcohol contaminated with impurities distils over at a higher temperature, and forms the tailings of the distillation. By the fractionation which occurs in the process the bodies of different boiling points are separated as much as possible, but a complete separation is not achieved, as volatile bodies, even with widely different boiling points.
always distil over with traces of bodies of different boiling points. Thus the first runnings always bring over a proportion of alcohol varying according to the perfection of the still, although the difference between the boiling points of alcohol and aldehyde is 55°, so that to be able to eliminate all traces of aldehyde a certain quantity of alcohol must be run off. This is set apart. As there is far less difference between the boiling points of propyl, butyl, and ethyl alcohols than there is between ethyl alcohol and aldehyde, the first two alcohols always distil over with the alcohol, but in such small proportions that they are negligible.

Testing the Purity of Alcohol.—Many methods have been recommended for the examination of industrial alcohol for impurities. Some of these are directed towards estimating the whole of the impurities, others only those of the first runnings, or of the tailings. It is certain, however, that none of these methods gives exact results, but each of them gives a good qualitative indication of the substance which they purport to detect. Amongst the first mentioned, the best known is that of Røeøe, based upon the solubility of fusel oil in chloroform, and that of E. Barjhet, in which the total impurities are indicated by the reduction of potassium permanganate. After this, Godefroy’s method, which, by the use of petroleum ether and sulphuric acid, separates the impurities of the first runnings and the tailings successively.*

The special reagents for the impurities in the first runnings are: ammoniacal silver nitrate, which is reduced; potassium hydrosulphate, which turns brown; sodium diazo-sulphanilate, which turns red—when brought into contact with aldehydes.

The impurities of the tailings are detected by concentrated sulphuric acid, which turns brown; by petroleum ether, followed by sulphuric acid, which causes the same reaction; and by aniline acetate, which turns red in the presence of furfural.

The problem of the estimation of the impurities in industrial alcohol is far from being solved, as much because of the varied nature of the bodies with which one has to deal, as because of the minute amount of each of them in a mixture where the whole quantity is often infinitesimal.

Smell and taste are almost always certain guides as to the purity of alcohol. One has only to dilute the suspected alcohol

* If exact results are required, text-books on analytical chemistry should be consulted.—E. J. P.
with water, and to evaporate a small quantity by friction in the palms of the hands, or to drop 1 gram of alcohol in a little boiling water and examine it. After a moment the smell of the fusel oil, if present, is readily distinguishable.

The presence of amyl alcohol is revealed by evaporating to half its volume a mixture of 10 grams of alcohol, with a few drops of a solution of potassium hydrate. The residue is then saturated with dilute sulphuric acid, and the presence of amyl compounds is detected by their characteristic odour. Without entering into the details of the process of rectification, the three following products are obtained from it:

1. The First Runnings of Alcohol.—A mixture of ethyl alcohol and aldehyde, which boils at a temperature below 78°.

2. Pure Alcohol, which in itself includes several qualities; whether it be drawn off immediately after the first runnings and contains traces of aldehyde, or whether it be drawn just before the tailings and already contains some of the impurities of a high boiling point. The alcohol distilled between these two products constitutes the middle runnings, and is finer and purer the further away it is from the two extremities indicated.

3. The Tailings.—Composed of a little ethyl alcohol with amyl and other alcohols of high boiling points. The essential oils (fusel oil) remain in the still with the water, and constitute the residues of distillation of the crude alcohol.

The art of refining consists in obtaining the greatest quantity of middle runnings possible. Therefore, the purest crude alcohol obtainable must be used, as from it more middle runnings and less first runnings and tailings will be produced.

Alcohol Determination.—It is of the greatest importance, to the seller as to the buyer, to know the real content of absolute alcohol in an alcoholic solution. The method employed is based on the difference of the specific gravity of water and alcohol, taking into account the contraction which takes place by mixing the two liquids. To ensure that this method is exact, it is necessary to be careful that the alcoholic mixture is composed of nothing but water and alcohol, as all other matters present will influence the specific gravity and lead to inaccurate results. We shall only treat in these pages of the mixtures of water and alcohol, which are found in commerce under the names of alcohol spirits, brandy, etc. The very small quantities of colouring matter, oils, and esters which are found, for example, in natural rum and cognac, do not exercise more than a slight influence.
PERFUMES AND COSMETICS

on the indications of the specific gravity, and may be neglected, as the errors which result from them are very slight.

The alcoholometer generally used in France is that of Gay-Lussac. The two extreme points of this instrument—0 and 100—indicate first pure water (0), secondly, absolute alcohol (100). The intermediate degrees show the percentage of alcohol by volume, that is to say, the number of cubic centimeters of absolute alcohol which are contained in 100 cc. of the liquid tested. The instrument being graduated at 15°, the readings are not true unless the liquid to be tested is at this temperature. If it is not, a table of corrections (an “excise” table) enables one to convert to its actual strength that indicated by the alcoholometer for a solution of alcohol of a different temperature. This table is usually provided by the makers of alcoholometers. It is not necessary to reproduce it here.

Tralles’s alcoholometer, used principally in Germany, corresponds to that of Gay-Lussac, used in France. In 1888 it was practically replaced by Richter’s alcoholometer (determining by weight instead of by volume).

The thermo-alcoholometers prescribed by the new law differ from the older ones in that the thermometer is not graduated on the Réaumur, but on the Centigrade scale, and also in that the scale records the alcohol by weight instead of by volume. The older instrument gave the percentage by volume of alcohol at 12-5° Réaumur, whilst the new one gives the percentage by weight at 15° Centigrade. This is an improvement which was necessary and advisable.

Change in temperature in a liquid causes a change in volume; but a kilogram is always a kilogram, and the calculation is simplified, both for excise purposes and for the manufacturer. This alteration ought to facilitate commercial transactions. The following table shows the relationship between the readings by weight of Richter’s instrument and those by volume of Tralles:—

<table>
<thead>
<tr>
<th>Tralles (volume)</th>
<th>Richter (weight)</th>
<th>Tralles (volume)</th>
<th>Richter (weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>70</td>
<td>62.5</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>72.5</td>
<td>65</td>
</tr>
<tr>
<td>12.5</td>
<td>10</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>20</td>
<td>16</td>
<td>75</td>
<td>68</td>
</tr>
<tr>
<td>30</td>
<td>24.5</td>
<td>80</td>
<td>73.5</td>
</tr>
<tr>
<td>40</td>
<td>33.5</td>
<td>85</td>
<td>79.5</td>
</tr>
<tr>
<td>42</td>
<td>35</td>
<td>83.5</td>
<td>80</td>
</tr>
<tr>
<td>50</td>
<td>42.5</td>
<td>89.5</td>
<td>85</td>
</tr>
<tr>
<td>60</td>
<td>52</td>
<td>90</td>
<td>85.5</td>
</tr>
<tr>
<td>65</td>
<td>57</td>
<td>200</td>
<td>100</td>
</tr>
</tbody>
</table>
NATURAL RAW MATERIALS USED

We do not labour the value of the modern instrument, but we direct attention to it because chemists and manufacturers are certain to meet with it in their work, with its new indications, and it is right that they should not come across it unexpectedly.

As we have already pointed out, alcohol is very hygroscopic, and forms with water several hydrates, with elevation in temperature and contraction in volume. Thus 53.9 volumes of absolute alcohol and 48.8 volumes of water do not yield 102.7 volumes of mixture, but only 100 volumes. These values correspond approximately with the formula $C_2H_4O + 3H_2O$. But outside this limit, further addition of water produces neither elevation of temperature nor contraction of volume. Fries's table, which is given on p. 10, is based on these facts.

This table is used in a simple manner. If one wishes to convert 95 per cent. alcohol into 85 per cent. alcohol, the column headed 95 per cent. is referred to, and the figure 85 per cent. into which it is desired to convert the alcohol is sought for in column 1. The figure corresponding to 85 per cent., which is found in column 2 (95 per cent.), is 13.3. This means that it is necessary to add 13.3 volumes of water to 100 volumes of 95 per cent. alcohol to convert it into 85 per cent. alcohol. Similarly, to convert 75 per cent. alcohol into 35 per cent. alcohol, it is necessary to add 117.8 volumes of water to 100 volumes of the alcohol.

**Absolute Alcohol.**—Alcohol of 96–98 per cent. strength is usually sufficiently strong for perfumery purposes and is obtainable commercially of a high degree of purity. But there are cases in which absolutely pure anhydrous alcohol is required. In such a case (the manufacture of Eau de Cologne, for example), the perfumer will be wise if he himself prepares such an alcohol from a concentrated alcohol derived from wine. But he should not use the ordinary method of dehydration, which consists of treating 96 per cent. alcohol with caustic lime. Alcohol so prepared has a flavour which is difficult to get rid of, and which defeats the required end. Anhydrous calcium chloride should be employed, which should be strongly heated just before being used. It is only thus that an absolute alcohol is obtained having the necessary characters.

**Fatty Bodies**

Neutral fatty bodies, which may be the products of animal secrptions or be derived from the vegetable kingdom, have in
<table>
<thead>
<tr>
<th>Alcohol</th>
<th>95 %</th>
<th>94 %</th>
<th>93 %</th>
<th>92 %</th>
<th>91 %</th>
<th>90 %</th>
<th>85 %</th>
<th>80 %</th>
<th>75 %</th>
<th>70 %</th>
<th>65 %</th>
<th>60 %</th>
<th>55 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>6.4</td>
<td>5.1</td>
<td>3.8</td>
<td>2.5</td>
<td>1.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>85</td>
<td>13.3</td>
<td>11.9</td>
<td>10.6</td>
<td>9.2</td>
<td>7.9</td>
<td>6.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>80</td>
<td>20.9</td>
<td>19.5</td>
<td>18.1</td>
<td>16.6</td>
<td>15.2</td>
<td>13.8</td>
<td>6.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>75</td>
<td>29.5</td>
<td>27.9</td>
<td>26.4</td>
<td>24.9</td>
<td>23.4</td>
<td>21.9</td>
<td>14.5</td>
<td>7.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>38.1</td>
<td>35.5</td>
<td>33.9</td>
<td>31.3</td>
<td>29.6</td>
<td>28.0</td>
<td>23.1</td>
<td>15.6</td>
<td>7.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>65</td>
<td>46.4</td>
<td>43.7</td>
<td>41.2</td>
<td>38.6</td>
<td>36.1</td>
<td>33.9</td>
<td>30.4</td>
<td>26.4</td>
<td>17.6</td>
<td>8.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>60</td>
<td>53.0</td>
<td>50.2</td>
<td>47.3</td>
<td>43.5</td>
<td>40.6</td>
<td>37.8</td>
<td>33.3</td>
<td>26.6</td>
<td>18.4</td>
<td>8.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>55</td>
<td>58.0</td>
<td>55.2</td>
<td>52.3</td>
<td>48.6</td>
<td>45.8</td>
<td>43.0</td>
<td>39.1</td>
<td>32.0</td>
<td>24.2</td>
<td>15.4</td>
<td>8.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>63.4</td>
<td>60.6</td>
<td>57.6</td>
<td>53.8</td>
<td>50.8</td>
<td>47.0</td>
<td>43.0</td>
<td>36.1</td>
<td>28.2</td>
<td>20.0</td>
<td>10.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>45</td>
<td>68.4</td>
<td>65.6</td>
<td>62.6</td>
<td>58.8</td>
<td>55.8</td>
<td>52.0</td>
<td>48.0</td>
<td>41.1</td>
<td>33.2</td>
<td>25.0</td>
<td>15.4</td>
<td>8.7</td>
<td>—</td>
</tr>
<tr>
<td>40</td>
<td>73.4</td>
<td>70.6</td>
<td>67.6</td>
<td>63.8</td>
<td>60.8</td>
<td>57.0</td>
<td>53.0</td>
<td>46.1</td>
<td>38.2</td>
<td>30.0</td>
<td>20.0</td>
<td>10.4</td>
<td>—</td>
</tr>
<tr>
<td>35</td>
<td>78.4</td>
<td>75.6</td>
<td>72.6</td>
<td>68.8</td>
<td>65.8</td>
<td>62.0</td>
<td>58.0</td>
<td>51.1</td>
<td>43.2</td>
<td>35.2</td>
<td>25.2</td>
<td>15.4</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Fries' Table for Calculating the Amount of Water Necessary to Convert 100 Volumes of Alcohol into Weaker Spirit
either case so much chemical and physical resemblance that they may be classed together. The importance of their employment in perfumery may now be instanced.

Neutral fatty bodies are (with exceptions which need not here be noted) compounds, known as esters, of the triatomic alcohol glycerine, with various fatty acids such as stearic, oleic, and palmitic acids, etc. Chemically pure neutral fats are glycerides, and are formed of varying proportions of stearine, oleine, palmitine, etc.

So long as the fatty acids belong to the same series, i.e. the saturated series, a given fatty acid, or its glyceride, will usually be more solid and have a higher melting point as the number of carbon atoms it contains increases.

Natural fats usually contain, besides glycerides, small quantities of free fatty acids, which have considerable influence on their taste and odour.

All are products of animal or vegetable origin, and are produced by the conversion of starchy matter into carbolic acid and glycerides. The fatty tissues of animals are found either immediately under the skin, as in the pig, enveloping the abdominal organs, or interposed between the muscular tissues. The medullary and cervical substance is composed of neutral fatty bodies. In vegetables, the fatty body is contained in the seeds and sometimes in the flesh of the fruit (olive oil, coco-nut oil). Animal fats are obtained by melting; vegetable oils and fats by pressure and by extraction. Cold pressure produces the best quality fat; by using a gentle heat the yield is increased, but the quality suffers. Whichever process of expression is used, hot or cold, the fatty bodies obtained will always contain a certain amount of water and impurities, which must be eliminated, as otherwise the fat would rapidly alter and become useless in the manufacture of perfumery.

Refining of Fats.—In the author's work on the manufacture of essences and perfumes a chapter was devoted to the preparation and refining of fats, to which the reader is referred. There are more modern and more efficient processes, but these processes can only be applied to animal fats, and to solid vegetable fats, and not to oils, which must remain liquid when used in manufacturing processes.

In order to avoid any considerable loss, the manufacturer may be content with a partial purification, which consists in placing a given weight in a copper heating vessel, adding to it
several pails of water, and heating it to boiling point after adding some ordinary salt. Impurities floating on the surface are then removed by skimming, the fire is withdrawn, and the liquid allowed to stand for several hours, when the clarified oil is decanted in the usual manner. To refine the oil further, that is, to bleach it without the employment of acids, the fat should be placed in a copper vessel, and 2 1/2 to 30 kilos. of water added for each 100 kilos. of fat, unless a direct steam jet is available, which is preferable to the use of water. The mass is heated until completely melted. The temperature being at about 75°, 3 kilos. of caustic soda lye (40° Béquimé) are added for each 100 kilos. of fat, and the temperature is raised to boiling point, with constant stirring. The mass is now in the form of a milky fluid. From 12 to 15 kilos. of refined salt are now added, which dissolves rapidly as the temperature is raised, and the liquid is well stirred; a mass of scum which is of a dirty grey colour and contains most of the more or less coloured impurities of the crude fat rises to the surface. After having slowed down the current of steam and withdrawn the stirrer, the small quantity of soap formed on the surface is removed. This is continually frothing and will overflow the boiling vessel if not frequently removed. If the scum is so light as not to be easily removable, a little salt added to the liquid will convert it into floating soapy masses, which are easily removed. The operation is completed when the scum has ceased to form, and in its place appears a light transparent froth.

The oil is then a transparent, pale liquid, and the steam should be turned off, the boiling vessel covered over, and the contents allowed to settle for at least one night. The saline liquid settles to the bottom and can be drawn off when desired.

There is, of course, a loss of fat in such a refining process. But products prepared with such a refined oil will probably keep much longer than those prepared with unrefined oils, and the improvement in the perfume more than compensates for the extra cost of refining.

Solid vegetable fats, as well as suet and lard, can be refined in this manner.

Fats obtained by extraction with organic solvents do not contain the same impurities as fats obtained by pressure. Sulphide of carbon and petroleum ether are the usual solvents employed.

Taken at a temperature of 15°, fats are either liquid, semi-
NATURAL RAW MATERIALS USED

solid (such as butter), or completely solid, such as suet, wax, or spermaceti.

All these substances are lighter than water, their specific gravity varying according to their age and method of preparation. They are insoluble in water, very slightly soluble in cold alcohol (with the exception of castor oil), rather more soluble in hot alcohol, and soluble in all proportions in ether, chloroform, carbon bisulphide, and essential oils.

They are not volatile, that is, they do not distil without decomposition. At a high temperature they decompose with the evolution of acrid vapour, due to the formation of acrolein. If the temperature be very high, they are decomposed with the formation of gaseous bodies which burn with a very luminous flame.

If they are treated under pressure with superheated steam, they are saponified. Saponification also results by heating with caustic soda, caustic potash, or ammonia.

The principal glycerides present in solid fats are stearine, palmitine, and oleine; the proportion of oleine is less as the melting point increases.

All solid fats liquefy at temperatures dependent upon the relative proportions of the glycerides they contain. In the same way, liquid fats deposit solid glycerides when they are cooled to a sufficiently low temperature. All oils become more or less turbid on cooling with the exception of the drying oils of the linseed type, which remain clear down to --15°.

The melting or solidification point of oils varies according to the age or method of preparation of the oil. Freshly-prepared fats have a sweet and agreeable odour and taste, and do not redden blue litmus paper. But under the influence of air and moisture, especially when kept in the light, they decompose, with the formation of free fatty acids. They then develop a sharp, acid taste and a disagreeable odour, and turn blue litmus paper red. The decomposition is, of course, only partial. The more volatile fatty acids are separated from their combination with glycerine and are responsible for the disagreeable odour and taste. The methods of removing these free fatty acids are those above described.

All fatty oils tend to thicken under the influence of air. Some of them, when exposed in thin layers, are converted into solid transparent layers, whilst others remain quite liquid, however thin the exposed layer may be. Those which solidify are the
so-called drying oils, with which perfumery is not concerned, such as linseed oil. Non-drying oils, such as olive oil, almond oil, etc., are those which are of interest to perfumers. There is a group of oils intermediate between the two, such as sesame oil, which for the purpose of the perfume manufacturer may be called "indifferent" oils.

Liquid Extracts—Oils

Olive Oil.—Olive oil is expressed either from the flesh of the olive, or from the entire fruit, including the kernel. But the oil obtained from the kernel is not identical with that obtained from the flesh of the fruit.

Provence, especially in the neighbourhood of Aix, furnishes the best olive oil. Lucca oil, and that obtained at Genoa and Nice, are the oils which may be described as second quality oils.

The mature fruits, separated from the kernels, are crushed and pressed. Virgin olive oil, the result of the first pressing, is clear and limpid and correspondingly expensive. Very high pressure furnishes a second quality, which is somewhat turbid and only becomes clear after sedimentation. A good quality oil is of a pale to golden-yellow colour, with a faint but sweet taste and slight, agreeable odour. It deposits solid glycerides at about 6°, and solidifies at about 1° to 2°. Inferior grades become solid at somewhat higher temperatures.

Second Pressings or Green Olive Oils.—The cakes of the first pressing mixed with over-ripe or bruised olives are digested with boiling water, and then, on cooling, pressed again. The oil thus obtained is turbid, deep yellow, or greenish in colour, and of a disagreeable odour, so that it cannot usefully be employed in perfumery. It can only be used for soap manufacture or other industrial purposes.

It is unnecessary to deal with bleached olive oil, which has no special employment in perfumery, and differs little from ordinary "first pressing" oil.

The latter is suitable for enflourage, that is, the obtaining of perfumes and essential oils from certain plants which contain them in only small quantities. It is also suitable for the manufacture of cosmetic oils, which will be dealt with in due course. Second quality olive oil is suitable for the manufacture of domestic soap, and sometimes even for toilet soap.

It will be readily understood that it is the finer qualities of olive oil which are more commonly adulterated. The perfumer
should therefore examine his oil most carefully. The oils most commonly used for the purposes of adulteration of olive oil are sesame, earth-nut (arachis), cotton-seed and especially poppy-seed. The elaidine test easily reveals the last-named oil, since olive oil, which is not a drying oil, is completely solidified by this reaction in eight to ten minutes, whilst poppy-seed oil yields a fluid mass even after a long time. But if one has to deal with arachis oil, detection of the adulterant is more difficult, and can only be relied upon by separating arachidic acid from the mixture, a process which must be carried out by a skilled analyst.

**Sesame Oil.**—The oil expressed from the seeds of *Sesamum orientale* makes an excellent substitute for olive oil. The first pressings are of a pale yellow colour, almost as pale as almond oil. It has no odour and its taste is sweet and agreeable. It thickens at +3°C and solidifies at -3°C. The oil is employed in perfumery, soaps-making, and in the ordinary enfluerage processes. Its use, however, is, unfortunately, limited by the fact that it resinifies somewhat rapidly.

**Almond Oil.** This oil is, *par excellence*, the best for the preparation of cosmetics. It is obtained by expression from the fruits of bitter and sweet almonds. It is of a pale yellow colour, a little more viscous than olive oil, but still perfectly fluid and completely inodorous. Its taste is agreeable and slightly sweet. Its specific gravity is 0.915 to 0.920. It commences to deposit at -10°C. It is soluble in 60 parts of cold and in 20 parts of hot alcohol. The oils obtained from the bitter and the sweet almond are identical.

**Peach Kernel Oil** is often substituted for almond oil. As the physical characters of these two oils are the same, it is necessary to apply a chemical test for detecting adulteration. A mixture of sulphuric acid and nitric acid gives a sufficient indication. Pure almond oil gives a practically colourless mixture, whilst peach kernel oil gives a pink coloration. If the mixture becomes a deeper red, sesame oil is probably present. To be certain of this, the following procedure should be adopted—mix 1 vol. of oil with 1 vol. of hydrochloric acid in which is dissolved a little sugar. The mixture is then well shaken. After standing for a few minutes the hydrochloric acid shows a well-marked red colour in the presence of even small quantities of sesame oil. The presence of olive oil is only detected by its odour, deeper colour or by chemical analysis.

**Oil of “Ben.”**—This oil is expressed from the nut known
under this name, of which the best variety is grown in Egypt—the more inferior in India. The latter is smaller than that from Egypt.

The oil is finer than almond oil and is not so liable to oxidation. It is of a yellow colour, odorous, and of exquisite taste. It does not congeal above +10°. Its specific gravity is about 0.910. It is used only for delicate enfluerage processes and the preparation of expensive cosmetics, and is difficult to procure.

Castor Oil is expressed from the seed of the castor oil plant, originally grown in India, but now found in most countries with a hot climate. The oil is obtained by expression, either hot or cold, of the deorcicated seeds. The first pressing, which takes place in the cold, yields very little, but the oil is colourless and very clear. The second pressing (hot) yields more, but the oil is more coloured and has a disagreeable taste. The second pressings can be improved by mixing the oil with an equal quantity of water, and boiling the mixture, allowing it to stand and separate, and then filtering the oil. Castor oil is intermediate between the drying and the non-drying oils. In very thin layers it solidifies almost completely. It is a colourless liquid, or at most slightly yellow, rather more viscous than most other oils, resembling a saturated solution of sugar in this respect, and has very little odour and an agreeable taste when freshly prepared. It becomes rancid on keeping.

Like olive oil, castor oil deposits solid matter on cooling and solidifies at —18°. On keeping, it becomes thicker and eventually resinifies. It is soluble in alcohol to a greater degree than any other fatty oil; and to a certain extent in petroleum ether, which it also dissolves. Its specific gravity varies from 0.950 to 0.970.

Castor oil contains three fatty acids not common to other oils, namely, ricinoleic, ricinie, and ricinostearic acids. Castor oil is used in soap-making, especially transparent soaps, to a considerable extent. The chemical examination of this oil yields excellent indications of its purity. Its easy solubility in alcohol is a safeguard against the addition of other fatty oils. Equal volumes of 90 per cent. alcohol and castor oil should be quite clear, but the presence of more than a trace of other oils renders the mixture turbid.

Neatsfoot Oil.—This oil is scarcely ever found to-day in a state of purity, most oils so called being factitious. The genuine oil is extracted from the hoofs of the animal. It is a semi-fluid
mixture at ordinary temperatures, in which solid stearin remains suspended in the liquid oleine. It does, not easily become rancid. When pure, it is useful in the manufacture of specially fine pomades, which are rendered more solid by the addition of a little paraffin wax. It possesses, however, no advantage over olive oil.

SOLID AND SEMI-SOLID FATS

Lard.—This fat, rendered from certain parts of the domestic pig, differs slightly in properties according to whether it has been obtained from the fatty tissues situated directly beneath the skin, or from the more internal fat layers of the animal. It is from the latter source that lard of the necessary consistency for pomades and certain soaps is obtained. Lard rendered by mixing the fat obtained from all the various parts of the body is not so useful in this respect as the lard rendered solely from the more internal tissues. The feeding of the animal has considerable influence on the character of the fat. Hungarian pigs, for example, fed mainly on acorns, yield a lard which is too soft for most perfumery purposes. In any circumstances, the manufacturing perfumer will be wise if he subjects the crude product as met with in commerce to a refining process such as has been indicated above, and he should only use a water-bath or steam to melt the lard, as otherwise he may impart to it the "cooked" taste which it so easily assumes when exposed to a naked flame.

A qualitative examination of this substance which is comparatively inexpensive, may be made in the following manner. A test-tube is half filled with the lard to be examined and melted on a water-bath. If the lard is pure, the liquid is quite transparent. If, however, it contains borax or similar adulterants, it will be turbid and will eventually separate into a transparent liquid with such impurities at the bottom of the tube. A rough and ready method of testing for the presence of water is to throw a small piece of the lard on to a red-hot coal. If water is present, a decoction, due to the rapid formation of water vapour, is easily discernible, whereas this is not the case with lard free from water. America exports large quantities of lard, which is often found to yield a reaction for cotton-seed oil. It is very rarely that this is due to adulteration, but it is the result of feeding the pigs on cotton-seed cake; the cotton-seed oil is absorbed, but leaves the resulting fat of the pig slightly contaminated, so that it yields the cotton-seed oil reaction.
Becchi has suggested the following method for testing lard. The fat is heated on the water-bath with an equal volume of an alcoholic solution of nitrate of silver for 7 or 8 minutes. If cotton oil be present, a brownish or even black coloration results, according to the amount of cotton-seed oil present. A more decisive test is to heat the oil in a solution of amyl alcohol with a solution of sulphur in carbon bisulphide. In the presence of cotton-seed oil a red coloration results (Halphen's reaction). It should be remembered that lard obtained from hogs which have been fed on cotton-seed cake, as indicated above, will yield these reactions. Salt is indicated by the formation of the easily recognised precipitate of silver chloride when treated with silver nitrate.

**Suet.**—The fatty secretions of ruminating animals are included in the term "suet." The term is usually qualified by the name of the animal producing it, as, for example, beef suet, mutton suet, etc.

The perfume industry is hardly concerned with any suet other than beef suet, and, for certain purposes which will be dealt with later, suet from the calf.

Beef suet is employed to some extent in the manufacture of toilet soap.

**Coco-nut Oil.**—The oil expressed from the flesh of the coco-nut (copra) is used in the manufacture of certain types of soap, but its use in other branches of the industry is limited.

**Cocoa Butter,** which is a quite different product from coco-nut oil, is obtained by expression from the deocarated and lightly roasted fruits of the cocoa bean (*Theobroma cacao*), which contain up to 50 per cent. of fat. It is a solid fat of a pale yellow colour, of specific gravity about 0.900 and melting at about 34° to 35°. It possesses a slight odour and flavour of the cacao bean, and does not become rancid by exposure to the air for a considerable period. It is soluble in ether, and if, when one part is dissolved in three parts of ether, the solution separates any solid matter, adulteration is certain. Equally, if 3 parts are dissolved in 2 parts of benzene, the solution should be perfectly clear.

Other fatty oils might be described, but as their employment in the perfume industry is limited, it is not necessary to discuss further this class of perfumery raw material.

**Antiseptics to Prevent Rancidity.**—All fatty bodies are more or less subject to become rancid. This must be guarded against, since, in spite of previous purification, rancidity may develop
and cause serious trouble. In order to obviate this, gum benzoin or benzoic acid may be used. Both these bodies possess antiseptic properties sufficiently strong to achieve the desired end, but as they have a distinct, although pleasant odour, their employment is limited. Salicylic acid is a most useful antiseptic, and as its price is now very low, it is very frequently used. Boric acid is also a most useful antiseptic, very low in price, without any odour, and sufficiently powerful to preserve oxidisable fats from turning rancid. Its use is rapidly becoming more general in the perfume industry.

**Lanoline.**—This fatty matter is obtained from crude wool, either by extraction by means of carbon bisulphide or from the waters used in de-fatting the wool. Liebrich was the first to recognise that this fatty matter was able to absorb more than its own weight of water, and, in the form of this stable emulsion, to be readily absorbed by the pores of the skin. The pure fat is of considerable value in the manufacture of pomades which are used on the skin. Well-purified lanoline keeps indefinitely without becoming rancid. As met with in commerce, it is yellowish or almost white, nearly odourless, in the form of an unctuous paste, neutral in reaction. It usually contains 25 to 20 per cent. of water, but may be obtained in the anhydrous condition. When containing water, it melts, and separates into two layers at about 40°. The lower layer consists of water, and the upper of anhydrous lanoline which sets to a yellowish, semi-transparent mass. When warmed, anhydrous lanoline will absorb 105 per cent. of its own weight of water, if the latter be well stirred in. Lanoline is, of course, not soluble in water, and only slightly soluble in alcohol. Its best solvents are ether, petroleum ether, and acetone.

A mixture of 80 per cent. of lanoline with 20 per cent. of cocoa butter is an excellent base for high-grade pomades, perfumed with delicate odours such as vanilla, rose, etc. Lanoline may be purified by washing with a dilute solution of soda. The free fatty acids are saponified, and a milky emulsion is obtained which can be separated in a centrifugal machine into two layers, the lower containing the soap, and the upper the lanoline, still slightly impure. A small amount of the soap is emulsified with the fat, and may be removed by adding a little milk of lime, which forms an insoluble soap which can be removed by washing the lanoline with water several times. To obtain an absolutely pure lanoline, the product is then completely dried, dissolved in acetone.
allowed to stand, the clear liquid drawn off, and the acetone removed by distillation. To this highly purified product 25 per cent. of water is added, and the lanoline is then the pure hydrous lanoline of commerce.

Lanoline must be kept in well-closed vessels and in a cool place, otherwise water will evaporate from the surface and the substance darkens and becomes coated with horny transparent matter.

**White and Yellow Wax.**—Beeswax is the substance produced by the ordinary bee to build up the skeleton of the honeycomb. After the honey is collected, the crude wax is melted in water, strained and cooled in appropriate moulds, either as bars or as small cakes. The colour of ordinary beeswax, which is of a varying yellow or brown, depends upon the food of the bee and the flower which furnishes the saccharine material. African and American wax, for example, are usually of a full brownish colour. Beeswax has a pleasant odour recalling that of honey. Its fracture should be dry and granular, with a chalky-white appearance (when adulterated with suet or similar substances the fracture is entirely different). The heat of the hand softens it; on mastication it does not tend to adhere to the teeth as is the case with wax adulterated with resin. Its melting point is about 60° to 64°. It is insoluble in water and in cold alcohol, but dissolves partially in ether and in hot alcohol. It is completely soluble in warm fatty and essential oils, petroleum ether, chloroform, and carbon bisulphide. Its specific gravity is from 0.960 to 0.970. Asiatic wax is a little heavier than most European specimens. When adulterated with suet, etc., the specific gravity is lowered.

To bleach wax, it is sufficient to melt the crude, pure wax on the water-bath and pour it into cold water in such a way as to allow it to solidify in thin strips, which are then exposed on linen cloths, when sunlight, air, and moisture will bleach it to an almost white colour. The wax is wetted frequently and turned over every six hours. Wax may also be bleached chemically, when the process is much quicker (by, for example, boiling a mixture of dilute sulphurous acid and calcium chloride with the wax), but chemically bleached wax is brittle and requires softening with at least 3 per cent. of suet. If suet is present to the extent of over 5 per cent., the addition is regarded by perfumers as an adulteration, and the wax would not be regarded as of good merchantable quality. White wax develops free fatty acids more rapidly than unbleached wax, and takes on a disagreeable odour.
which it communicates to any other fatty matter with which it may come in contact. Unless its use be regarded as absolutely necessary, white wax should, therefore, not be used in perfumery.

From the chemical point of view beeswax is a mixture of about 20 per cent. of free cerotic acid with 80 per cent. of esters in which glycerine, the usual alcoholic constituent of fats, has been replaced by myricyl anderyl alcohols. It is this absence of glycerine that causes burning beeswax, if pure, to be free from the odour of acrolein, which is characteristic of glycerides when burned.

Beeswax is often adulterated. The principal substances used for sophistication are Japan wax, paraffin wax, resin, stearine, and suet. Very rarely one meets with adulteration with starch, ochre, or other mineral matter. This is easily detected by dissolving the wax in hot turpentine, when, instead of obtaining a clear solution, an insoluble deposit is yielded, varying in appearance with the nature of the adulterant. We have already pointed out that the presence of resinous matter is detectable by the peculiar adherence to the teeth on mastication, which is not the case with pure wax.

Spermaceti. This waxy substance is formed in the orbital cavities of the head, as well as in a kind of medullary tube situated under the skin, of various species of whales, especially the so-called sperm whales, and to a small extent the dolphins of the South Polar seas; this medullary tube commences in the interior of the head and is prolonged as far as the termination of the spinal cord in these mammalian sea animals, large quantities of spermaceti being obtained from a single animal. It occurs as a solution and suspension of the solid spermaceti in a true liquid oil, sperm oil. Spermaceti separates on cooling the oil as a mass of small crystals, which are purified by repeated washing with alkali (a dilute solution of potassium carbonate), and then remelting and solidifying in ingot or saucer-shaped moulds. When pure, spermaceti forms a very white mass with a brilliant, lacereous and crystalline fracture. It has a faint, indescribable odour and an agreeable fatty taste. Its specific gravity is about 0-943 and melting point 45–50°. It does not stain unglazed paper. It is soluble in 7 parts of warm alcohol, or in 35 parts of cold alcohol; and is readily soluble in ether, chloroform, or carbon bisulphide. It is, however, but slightly soluble in petroleum ether.

Spermaceti consists, in the main, of cetyl palmitate. It is employed to a fair extent in perfumery, chiefly in the manufa-
PERFUMES AND COSMETICS

ture of solid préparations or “concretes.” It may not, therefore, be without interest to direct attention to its more common adulterants.

If stearine be present, the fracture will be more conchoidal, and the texture more granular. As stearine usually contains free stearic acid, when a spermaceti so adulterated is mixed with a boiling solution of potassium carbonate, effervescence will result due to the evolution of carbonic acid gas, which is not the case with pure spermaceti. Such is indicated by the permanent stain produced on unglazed paper, and by the odour evolved on heating.

Liquid Hydrocarbons—so-called Mineral Oils. The oils known as mineral oils have been in use for many years; they consist of mixtures of various hydrocarbons of natural origin, found in various parts of the world, sometimes as oil only, sometimes mixed with water. They were not, at first, used to any except a small extent for burning, lubricating, and medicinally but as their value for these purposes became more recognised by the continued work of the petroleum technologists, their employment increased correspondingly. To-day the mineral or petroleum oils form an exceedingly important group of commercial substances, which may be referred to here, as they have a certain use in perfumery.

Crude petroleum, such as is obtained in America, is certainly a product of a natural “dry distillation;” that is, it is formed by the action of heat on organic matter, causing it to decompose in the absence of air. Its formation is due to the heavy deposits of marine algae, etc., in prehistoric times buried and altered in the terrestrial deposits, as a result of geological changes, and which, under the action of the earth’s internal heat, yielded the hydrocarbon products. Pennsylvania, Canada, and Virginia in the Western Hemisphere, Baku, on the Caspian Sea, and Galicia are areas which produce very considerable quantities.

The liquid at first gushes from the well, but when the accumulation of compressed gas has ceased, it must be raised, and mixed with water of a greenish colour, and disagreeable odour, by means of very powerful pumps. It is then allowed to settle in enormous tanks, when it separates into an aqueous layer and a layer of crude petroleum. The latter is submitted to a series of fractional distillations and a whole series of hydrocarbons, of different boiling points, is obtained. Each fraction thus obtained is a mixture of several distinct hydrocarbons.
Prelateum ether or naptha is the earliest fraction collected. It distils between 40° and 70°, and is used as a solvent for the extraction of certain essential oils and perfumes. Its specific gravity is about 0·665, and it evaporates with the warmth of the hand and has hardly any odour, especially after being rectified. Benzene is of a higher boiling point, about 80° to 100°, and has a specific gravity about 0·690 to 0·705. It has but little odour when well rectified, and is used in the extraction of fats, the cleaning of cloth, and in the perfume industry for the purpose of utilising residual fatty matters. Ordinary cleaning petroleum boils between 120° and 130°, burning paraffin between 150° and 250°, and mineral lubricating oils at temperatures much higher than these. The still higher boiling hydrocarbons are left in the still and are known as soft petroleum, or petroleum jelly.

Petroleum jelly is simply a variety of paraffin, less solid and of lower melting point. It is obtained by heating by steam the impure petroleum residues to about 30°, when sufficiently soft shaking with 10 per cent. sulphuric acid (60° Béaume) and finally leaving it to settle. The layer of oil obtained is heated to 80°, and 10 per cent. of its weight of dry animal charcoal is added. It is then clarified by decantation, and filtered through a steam-heated charcoal filter. It becomes whiter each time it is filtered. The clear oil, free from tarry matter, is transferred to a copper vessel where it is heated by steam to 250°. A sample taken after about two hours indicates whether the operation is finished.

The steam is then shut off, and it is filtered once more, and is then ready for use. It is now a clear semi-transparent substance, of a buttery consistence, with a specific gravity about 0·885, odourless and tasteless.

Thus prepared, petroleum jelly should not turn brown when mixed with concentrated sulphuric acid and warmed for twenty-four hours on a water-bath, and thoroughly shaken from time to time.

Another test is to replace the sulphuric acid by a small fragment of sodium. This metal will rapidly lose its characteristic brightness if the petroleum jelly still contains sulphur or oxygen compounds.

Boiling alcohol brought in contact with the petroleum jelly should not turn litmus paper red; if it does so, it indicates the presence of sulphuric or organic acids.

Paraffin.—Although paraffin is simply a mixture of hydrocarbons more solid and of higher melting point than petroleum jelly.
the name is used for similar bodies which are found dissolved in the residues of the dry distillation of the hydrocarbons of tar, lignite, and peat. They are also contained in the residues of petroleum, but in such quantities that it is not always worth the cost of extracting them, as a 10 per cent. yield is necessary if the extraction is to be worth while.

The best lignites for obtaining this material come from Saxony. The south of Hungary also yields a bituminous schist, which yields a considerable quantity of solid paraffin.

The first product from the distillation of lignite is a fairly clear brown oil which on fractional distillation first yields burning oils, etc., and it is not until over 200° that oil containing solid paraffin is obtained.

Mineral oil which is treated successively by sulphuric acid and solution of caustic soda is decolorised, and eventually, when sufficiently cooled, deposits brilliant flakes of solid paraffin.

The use of centrifugal force and high pressure removes practically all the adherent oil from the solid matter. This is remelted, poured into moulds, and is then ready for use. It is a white, semi-transparent mass, with very little if any odour, unctuous to the touch, and melting at different temperatures according to the fraction of the substance dealt with.

To obtain solid paraffin completely odourless and tasteless, it should be dissolved in a suitable solvent and recrystallised, but this is seldom done. It is insoluble in water, only slightly soluble in boiling alcohol, but easily soluble in ether, petrolatum ether, carbon bisulphide, and fatty oils. It is not attacked by acids of alkalies. Its melting and boiling points vary over a wide range. It consists of a mixture of hydrocarbons, the melting and boiling points of which rise with the number of carbon atoms they contain.

It is used in the preparation of various creams, lip-salves and similar substances. It is very useful in rendering corks impermeable to liquids.

Ceresine, Mineral Wax, or Ozokerite.—This form of paraffin is found in fairly large quantities in the schists round about the neighbourhood of petroleum wells.

Galicia, Hungary, Baku, and various districts of North America are the principal sources of this material. It is submitted to a preliminary melting to remove mineral matter, which often reaches as much as 15 per cent. in the raw material. By distillation, a yield of about 75 per cent. of oil is obtained,
which deposits the solid ceresine on cooling. The remainder of
the purification is carried out as in the case of ordinary paraﬁn.
If the last traces of colour and odour are to be removed, it is
best to use a little blood charcoal. The yield of reﬁned ceresine
is about 25 per cent. of the raw material. It is a waxy substance
of amber colour, inodorous, with a ﬁne granular fracture, very
similar in appearance to yellow beeswax. Its melting point
varies over a fairly wide range. In a pure state, it will only
darken sulphuric acid to a brown colour. It is quite unsaponiﬁ-
able, as it consists of hydrocarbons.

All the bodies of this series, being hydrocarbons, do not
oxidise in the air, hence their employment in perfumery where
it is possible to substitute them for more easily alterable bodies.
But they are not so readily absorbed by the skin as the true fats,
nor do they ﬁx perfumes so well as vegetable oils do. They are
useful in the extraction of perfumes, but are not to be greatly
recommended in the manufacture of cosmetics.

Essential Oils and Perfumes

Essential oils and other types of perfumes extracted from
plants will not be dealt with to any extent in this work, as they
are fully treated in other special volumes.

Full information will be found in these special volumes as to
the physical and chemical characters of the essential oils, the
composition, the presence and development in the plant, and
their method of extraction by distillation, expression, maceration,
enfleurage, and by the use of volatile solvents. In the works by
the authors referred to, distilled aromatic waters, tinctures, and
extracts have been described, as well as the principal apparatus
used in their manufacture. A few words on terpeneless oils,
however, may be of interest. Most essential oils contain, in
addition to their real odorous constituents, a certain quantity of
terpenes, hydrocarbons which do not contain any oxygen, and
which are practically valueless from the odour point of view.
They are only slightly soluble in alcohol, and easily oxidise and
develop a disagreeable odour. They are, therefore, useless from a
perfumer’s point of view. Lemon and orange oils contain 90 per
cent. or more of their weight of terpenes; bergamot, lavender,
geranium, and other oils contain less, but varying quantities of
terpenes, and some contain none or only small quantities.

— "Fabrication des Essences et des Parfums," J. P. Durvelle; "The
The introduction of terpeneless essential oils into commerce was first due to H. Hensel, who removed the terpenes from various oils, leaving a mixture of practically all the oxygenated constituents which form the odour value of the oil.

Many oils also contain sesquiterpenes, higher boiling hydrocarbons than the terpenes, but which have similar characters and may also be removed with advantage.

The removal of the terpenes and sesquiterpenes is effected by fractional distillation under reduced pressure, but Cerbeland considers that a useful terpeneless oil of lemon may be prepared in the following manner. The oil is well shaken for several hours with 45 per cent. alcohol; the oxygenated soluble constituents which are the odour bearers dissolve in the dilute alcohol. The liquid is then allowed to separate, and the terpenes are removed. These can be used in conjunction with citral for cheap soap perfumery or similar purposes. The alcoholic solution is then freed from alcohol by distilling it off; leaving a concentrated lemon oil sufficiently free from terpenes to be used as terpeneless oil.

In practice, however, the terpenes are removed as above indicated by fractional distillation. The yield varies considerably in a given oil. Oil of lemon, on the average, yields about 5 per cent. of terpeneless oil. The terpenes, of the chemical formula C_{10}H_{16}, are characterised by a lower boiling point than most of the oxygenated constituents and by a low specific gravity. The sesquiterpenes, of the formula C_{15}H_{24}, on the other hand, have a higher specific gravity than the terpenes, and a boiling point which is frequently higher than those of the oxygenated constituents. Both series of hydrocarbons are practically insoluble in dilute alcohol, and have only a very slight odour and a strong tendency to oxidise and resinify under the influence of air, light, and moisture. The numerous terpenes resemble each other closely in odour and taste, so that they have little effect in determining the character of an essential oil. Thus pinene is found in all varieties of turpentine oil, in camphor oil, in coriander, fennel and star aniseed oils, and in many others. Limonene is present in lemon, orange, bergamot, and pine-needle oils. Phellandrene is found in eucalyptus, pine-needle, and star aniseed oils, etc. The terpenes, having but a slight odour themselves, but still a distinct one, tend to mask the odour of the oxygenated constituents. They are far less suitable as a diluent than alcohol, because they are so easily oxidisable; and there is the further
point to be considered, namely, that they are present in very variable amounts in the same type of oil. These variations are due to differences in climate, soil, humidity, greater or lesser sunlight, in the same way, for example, as the wines in different districts vary in alcoholic strength. But with terpeneless oils, these objections disappear. The products are always nearly identical, even when prepared from different years' oils. The principal advantage in the use of terpeneless oils is their solubility in dilute alcohol, which allows the preparation of relatively strong perfumes with weak alcohol.

Further, essential oils gain in delicacy of odour by the elimination of the terpenes. For example, geranium oil, even of the finest quality, is only slightly improved by the addition of otto of rose—the geranium odour still predominates. But a small addition of otto of rose to terpeneless oil of geranium will give it a characteristic rose odour. Italian Neroli oil is not very fine in odour and, when mixed with French oil, lowers its odour value; but when in the terpeneless condition the two oils can be mixed in equal proportions without lessening the odour value at all. Spike lavender oil freed from terpenes has an odour which, although not so fine, approximates to that of genuine lavender.

Terpeneless Japanese peppermint oil is nearer in value to the corresponding American oil than is the case with the natural oils, and American oil, well rectified and rendered terpeneless, approximates in odour value to the corresponding English oil. A few simple experiments will show the perfumer the accuracy of these relationships.

The following table indicates the difference in the odour values of the natural and the terpeneless oils:

<table>
<thead>
<tr>
<th>Oil</th>
<th>Strength of Terpeneless Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bergamot</td>
<td>2.5 times that of natural oil</td>
</tr>
<tr>
<td>Cananga</td>
<td>10-13</td>
</tr>
<tr>
<td>Cedar</td>
<td>6-10</td>
</tr>
<tr>
<td>Lemon</td>
<td>20</td>
</tr>
<tr>
<td>Cypress</td>
<td>30</td>
</tr>
<tr>
<td>Absis species</td>
<td>17</td>
</tr>
<tr>
<td>Limes</td>
<td>12-15</td>
</tr>
<tr>
<td>Mandarin</td>
<td>60</td>
</tr>
<tr>
<td>Italian Neroli</td>
<td>2.5</td>
</tr>
<tr>
<td>Opoponax</td>
<td>4-5</td>
</tr>
<tr>
<td>Patchouli</td>
<td>4-5</td>
</tr>
<tr>
<td>Peppermint</td>
<td>1-5-2</td>
</tr>
<tr>
<td>Orange</td>
<td>50-60</td>
</tr>
<tr>
<td>Rosemary</td>
<td>3-5</td>
</tr>
<tr>
<td>Thyme</td>
<td>2-5-4</td>
</tr>
<tr>
<td>Balsam of Tolu</td>
<td>3</td>
</tr>
<tr>
<td>Juniper</td>
<td>20</td>
</tr>
</tbody>
</table>
PERFUMES AND COSMETICS

We may now direct attention to a few aromatic substances which are of the greatest importance to the perfumer: these are musk, civet, ambergris, vanilla, and mastic. The perfumer uses these without the interaction of any previous industrial treatment of them.

Musk.—The musk deer, *Moschus moschiferus*, is found on the higher slopes of the chain of mountains which traverses Central Asia from the borders of Central Siberia to the termination of the Himalayas (the plateaux of Tibet, Tartary and the interior of China, etc.), in regions covered with perpetual snow. This animal, which is very beautiful in appearance, is not horned as are the deer of our own climates. The male, when arrived at the age of puberty, "bears, in the centre of the abdomen, between the navel and the organ of generation, a gland imbedded in the epidermal tissues. It is in this gland or "pocket" that the musk as we know it is contained. From the zoological point of view, there are many deer of this family, but only two or three varieties furnish this valuable perfume material, of which the price is very high. There are *Moschus moschiferus*, *M. alticus*; and *M. sibericus*. Sometimes the deer are hunted with the gun, sometimes caught in traps, when they are deprived of the musk pocket, attached to a small portion of the skin of the abdomen, and this musk pod, as it is afterwards called, is then dried. In the fresh state, the matter contained in the gland is soft and unctuous, but on drying assumes the consistence which allows of granulation into the form in which we meet it in commerce. There are several varieties of musk, the prices of which vary considerably. The principal variety—which constitutes 85 per cent. of the total musk of commerce, is Tonquin musk, which is the most valued of all. The pod is almost spherical, from 1 to 1½ inches in diameter. The surface which is attached to the muscular tissues is smooth and devoid of hairs, whilst the external surface is covered with hair, resembling a miniature beard, converging towards a central opening. The muscular skin of the pod is easily separated from the skin of the abdomen. It is of a pale to deep brown colour, and within it is found the musk itself. It is a brownish mass, somewhat greasy, but very friable, and when crushed forms grains of small size. The mass is traversed in every direction by a thin pellicle, and quantities of hairs are often met with. The odour is quite distinctive, and almost unsupportable to many people. It is very penetrating and exceedingly persistent. It is only when used in minute quantities
that it becomes an agreeable perfume: Its taste is bitter and
sharp. Pods of Tonquin musk weigh from 15 to 40 grams and
contain about 50 to 60 per cent. of their weight of true musk.
Genuine musk, as met with in commerce, contains about 15 per
cent. of moisture and yields 8 per cent. of ash. To water, it
yields about 50 per cent. and 10 to 12 per cent. to alcohol. It
contains about 2 per cent. of a ketone, museone, to which it
principally owes its odour.

Tonquin musk comes principally from the deer hunted in
Tonkin China, Thibet, Mongolia, and Cashmere. Canton and
Shanghai are the principal ports of shipment, and the principal
markets for it in Europe are London and Paris. A catty, as the
package is called, contains about 25 pods, each carefully packed
in a kind of silk paper covered with Chinese characters. These
catties are about 6 or 7 inches long, 4 inches wide and deep. As
many as 2000 catties of 600 grams each have been exported in
one year from Shanghai. For some years past a special type has
been exported under the name of Yuman musk. The pods are
almost spherical, covered with but little hair, and contain a
yellowish musk of very fine odour. There is a Yuman variety
known as "Tamp'i," in which the pods have been deprived of
the ring of abdominal tissue found in other varieties. It is
generally understood that the contents of these pods have been
tampered with. There is a much-valued variety of Tonquin
musk known as Blue Skin musk. Here the two or three layers
of outer skin have been removed, revealing a membrane of
bluish colour, which gives its name to the musk. It is more
easily dried and is always treated more delicately in Shanghai
than other varieties, and as it contains a greater percentage of
actual musk, on account of the removal of some of the skin, it
naturally commands a higher price.

Cabardine or Siberian musk has not the same value as Tonquin
musk. It is collected on the plateaux of the Altai range, in
Central Siberia and in Mongolia, and the exportation until its
present disorganisation was always carried on through Russia.
A certain amount found its way to China and a certain amount
reached the London market, from which sources Europe obtained
its supplies. The pods are more oblong than those of Tonquin
musk, the under skin is of a dirty yellow colour and very brittle
and hard, whilst the upper skin is covered with grey hairs, ter-
minating in white points, as though they had been cut with a
razor. The opening of the pod is situated nearer the edges than
in the Tonquin pods. The musk itself is more transparent, soft in the natural state, easily powdered on drying. The pods weigh from 15 to 30 grams and the perfume, although less intense, resembles that of castor. An aqueous extract of this musk gives an abundant precipitate with a solution of mercuric chloride, but this could hardly be relied on as a distinctive test. Assam or Bengal musk resembles Tonquin musk in texture. The pods are usually larger and are frequently attached to pieces of skin of the abdomen. The pairs are of a reddish-brown colour. The perfume is less intense, and rather resembles that of Siberian musk. About 200 pods are packed in small iron or wooden boxes for export. Bokhara musk is hardly a commercial article in Europe. It is rarely met with, and is in the form of small pods about the size of a pigeon’s egg. The odour is very weak; only a few hairs of reddish colour are on the skin, and the lower skin is greyish-black.

Apart from the true musk, or product of the musk deer, we may mention the “American” musk, or musk from the musk rat, *Fiber zibeticus*. This substance, not found in commerce to any extent, is the product of a gland attached to a caudal appendix of the animal. It is obtained by cutting up the gland into small pieces and slaked lime—4 grams to each gland—is mixed with the tissues. The whole is macerated in alcohol, and an infusion is thus obtained, after a fortnight’s maceration, which is claimed to be at least three times as powerful as a corresponding extract of true musk, and the odour value of which is midway between those of Tonquin and Sumboul musks. Although practically unknown in England, there is said to be an increasing trade in a musk derived from the female alligator. This animal is provided with four perfume-secreting glands, two in the head under the throat, and one on each side of the abdomen. The “musk” occurs as a very thick paste, yellowish in colour, and of a distinctive, penetrating odour which the natives of Brazil call “lizard odour.”

The composition of musk varies, even when pure, very greatly according to the age of the deer and the food he has eaten. Besides various mineral salts, it contains astringent substances, cholesterol and ammonium carbonate (the last named probably as a decomposition product). The perfume of musk, so far as is at present known, is due to the presence of small quantities of two ketones of unknown constitution which, are present to the extent of from 0.5 to 2 per cent. Of these, the principal is
muskone, a thick, colourless oil of the formula C₁₅H₂₁O (or C₁₅H₂₀), having a powerful musk odour. It boils at 327° to 330°, and may be regarded as the principal odour-bearer of natural musk. This odour is, of course, modified by the gradual decomposition of musk which takes place on exposure to air and moisture, when ammoniacal decomposition products are formed.

Water, as above stated, dissolves about 50 per cent. from musk. The aqueous solution is slightly alkaline to litmus. Absolute alcohol dissolves from 10 to 15 per cent., or rarely, a little more. Dilute alcohol dissolves more, in proportion to its dilution with water. Ether and chloroform only dissolve a very small amount.

Musk is one of the most important raw materials for the perfume industry. Although in its natural state its odour is revolting for most people, it is, when used in very small proportions with numerous essential oils, able to impart intensity and lasting properties which they lack by themselves. An enormous number of the best perfumes contain musk, but the art of the perfumer is to know how to employ minute quantities which lose their characteristic odour whilst greatly modifying the odour of the other ingredients. Unless careful judgment in this direction is used, the powerful perfume of musk will predominate and overcome all other odours, and the final "bouquet" will not be what was expected. Musk is employed in the form of an alcoholic extract (80 per cent. alcohol). It is well to add a few drops of ammonia to the alcohol.

The Adulteration of Musk.—The high prices paid for musk are an inducement to sellers to adulterate it, especially the Chinese sellers, who are masters in the art of adulteration. It is especially easy for them, as they have the product in its fresh state and the time and opportunity to manipulate it. Sometimes they abstract some of the pasty musk from the pod, sometimes they introduce through the opening in the pod foreign matter which can be mixed with the genuine contents, such as congealed blood, earthy matter such as powdered ochre, or even lead shot to increase the weight.

When powdering, it is necessary to examine the outside of the pod, in which any cut or tear should at once arouse suspicion. When the pod is opened, the contents should be examined, when particles of lead or sand, if present, may be observed. The pure substance should have a characteristic granular appearance, and when a small fragment is ignited on platinum, no odour of burnt...
horny matter should result. A solution obtained by digesting 12° per cent. of musk in distilled water should become turbid on the addition of solution of mercuric chloride, but should not yield more than a minute precipitate (except in the case of Siberian musk). If a copious precipitate results, the presence of ammonium carbonate or Siberian musk is probable. Grain musk is so subject to adulteration that the perfumer 'should' never purchase it except from firms whose integrity is well established. The empty pods have a perfume value, and are dealt in and used for the preparation of second-grade musk tinctures, etc.

The odour of musk is so penetrating and so lasting that any one using it should not touch it with his fingers, but use a spatula or similar contrivance. Equally, it should never be placed on a bare scale pan, but should be weighed into a tared glass vessel.

Camphor, mustard oil, or even solid gold attract and retain the perfume of musk. If one desires, after finishing using musk, to remove the odour from one's hands, it is useful to add a little solution of camphor in alcohol, or a little mustard flour to the water in which the hands are washed, when the odour will be entirely or nearly entirely removed. Artificial musk will be referred to in the section dealing with artificial or synthetic perfumes.

Civet.—Civet is the secretion of a double gland found in both sexes of the Civet cat, which are species of the animal Viverra, small, cat-like animals of the tiger species. The glands are situated close to the sexual organs. Two species are principally responsible for the production of civet, Viverra zibeta, of Asia, found in India, on the Persian Gulf, etc.; and V. civetta, of Africa, found in Egypt, Abyssinia, Nubia, Cordova, and, rarely, in Central Europe. Some of these animals become fairly tame on keeping, others remain somewhat savage, and they are kept in long, narrow cages so that when the secretion is removed from the gland, which is usually done twice a week, the animal cannot turn his head round sufficiently to attack the operator. The animal is often purposely worried and irritated for a short time before the operation, as this causes an increase in the amount of the secretion, which is then placed in empty horns and exported. A small amount is produced in Central America from animals which have become acclimatised there.

Fresh civet is a yellowish mass, soon becoming brown on the surface, of the consistence of butter. Its odour may be described as faecal, and is intensely disagreeable, more so than musk, which
NATURAL RAW MATERIALS USED

it resembles. It is like musk, only in an extremely dilute condition that it can be used, not only as a fixative, but to modify other odours.

Sack quite recently isolated a ketone from civet which is the principal, or one of the principal, odour-bearers present. He has termed this Zibethone. It is a liquid boiling at 342°. Skatole is also present, and is largely responsible for the faecal odour of civet.

Castor.—This body is now so little employed in perfumery that it need only be referred to. It is a secretion obtained from the beaver, having an odour recalling that of dilute musk with a suggestion of birch tar and pine resin.

Ambergris is a valuable raw material of perfumery, found in masses of various sizes floating on the sea. It is probably the product of disease of the whale Physalian macrocephalus, a cosmopolitan animal, but principally met with near Madagascar, Surinam, Japan, etc. A certain amount of ambergris is obtained by hunting the whale and extracting the ambergris before it has been rejected by the animal. It is generally more profitable to seek for floating ambergris in stormy weather, when the lumps are washed up towards the shore. It occurs in irregular, opaque, friable lumps of pronounced waxy appearance. The colour is grey to brownish, and in the smaller pieces the variations in shade are characterised by a fairly regular stratification. It is nearly tasteless, and softens at 25° to 30°. It can easily be pierced by a needle, an operation which is useful in controlling the purity of the substance. When the needle is withdrawn, it should have nothing adhering to it, whereas if resinous matter has been added, some of the substance sticks to the needle. The fracture is fine, granular, and slightly laminated. The odour is characteristic, but weak, reminding one somewhat of benzoin. It is very persistent and develops to a marked extent by a rise in temperature. Ambergris melts in boiling water, forming an oily layer floating on the surface. It burns without leaving more than traces of ash. Its specific gravity varies, usually, between 0.900 and 0.920, and its melting point is about 40°. Large pieces of ambergris should be regarded with suspicion. They often contain the bones of cuttlefish and other sea animals.

Ambergris is easily dissolved by ether and fatty oils, leaving very little residue. It is less soluble in alcohol, even at an elevated temperature. Various grades of ambergris exist. The most appreciated is of a clear grey colour, brown or white varieties.
being less esteemed. Being very expensive, it lends itself to adulteration, one of the commonest forms being the addition of gummy or resinous particles of similar appearance.

Rihan in 1912 examined the crystalline substance found in ambergris by Pelletier and Caventou, which is known as ambreine. He found that it was not a single substance, but on purification he obtained pure ambreine melting at 82°. Further than this, no other substance, except, perhaps, benzoic acid, has been identified in this perfume material. Ambergris should be stored in glass or metal vessels kept well corked. In preparing alcoholic tinctures of ambergris, greater strength will be obtained if a small trace of potassium carbonate be mixed with the ambergris and allowed to stand for a little while before the alcohol is poured in. Ambergris is not so much an actual perfume substance as, like musk and civet, to fix and improve other perfumes which are delicate and fugitive.

Vanilla.—This substance is the fruit, properly dried and cured, of a climbing orchid, a native of Central America, and which has been acclimatised in Bourbon (Réunion), Jamaica, the Seychelles, Java, Tahiti, Mauritius, and the Fiji Islands. There are two species in cultivation for the production of this spice, Vanilla planifolia, the true Mexican vanilla, and V. pompona, the West Indian vanilla. At the end of the flowering, a long, thin, unicellular pod is formed which does not ripen the first year, and which attains a length of as much as 8 to 9 inches. The pods are collected before they are quite ripe, dried by various methods, and cured either in the sun or by artificial heat and packed in bundles ready for delivery to users. Whilst the flowers in their natural state are freely fertilised by bees, etc., the cultivated plant is not so fortunate, and hand fertilisation has invariably to be resorted to. The immature pod or bean contains a milky juice of bitter taste, which is probably responsible for the toxic effect on consuming them. On drying and curing, this latex is converted into a semi-solid, brown mass, almost black, which contains the flavouring principles of the bean. If allowed to reach maturity on the plant, the pods open and eject their contents. This is, partly, the reason why they are gathered before ripening. When gathered, they are exposed to the sun, which soon dries the outer skins. They are then exposed in heaps in linen or woollen cloths, for example, sprinkled with water, and again dried either by the sun or by artificial heat, the pods being continually shaken backwards and forwards. The
pods turn brown and the latex is converted into an aromatic, pasty substance. An experienced workman knows when to stop the process at the right time so as to prevent a too energetic fermentation spoiling the earlier results of the process.

In certain districts, Réunion, for example, the pods are steeped for about twenty seconds in water at 90°, heaped up, and left to dry by natural heat. In this case, the operation is stopped at a definite time after the outer coat has become brown. The cloths are opened, and the pods turned out on tables, where they finish the drying process. They are then sorted out according to their lengths, tied in bundles of about 60, and packed in tins of 20 bundles. Good quality vanilla has a dark brown colour, with a thin skin, greasy to the touch, easily bent, and curled at the ends. The pods are flat, striated in the direction of their length, from 4 to 9 inches long, and about 1/4 to 1/2 inch in breadth. The matrix in which the numerous black seeds are imbedded should be very abundant in quantity and very aromatic in quality. A pod which is broken and empty is valueless.

Placed in well-closed receptacles, and kept at a temperature of 28° to 30°, vanilla of good quality (except certain types) becomes covered with a white, crystalline crust, very delicate in appearance, and very sweet in odour. These crystals are pure vanillin. Many lower qualities become similarly coated, and occasionally one meets with cases where low-grade vanillas which will not "crystallise" are treated with an alcoholic solution of either vanillin or benzoic acid, to simulate the natural crystallisation. Vanillin, the principle which gives most of its odour to the bean, is chemically, methyl protocatechuic aldehyde. It exists together with a number of other unknown aromatic substances, which together impart to the vanilla bean its characteristic odour and flavour. For this reason, artificially prepared pure vanillin does not completely reproduce the odour and flavour of the natural bean.

The aromatic portion of vanilla is soluble in fatty and essential oils, as well as in alcohol. Sometimes one finds in commerce exhausted vanilla beans which have been smeared with a thin layer of balsam of Peru, and then dusted with benzoic acid, so as to give them some resemblance to the genuine article. But if one presses these beans lightly between two sheets of paper, the latter become stained at once, thus revealing the adulteration. Some poor-looking beans are doctored in Mexico by giving them a coating of a dark-coloured oil.
The contents of the pod contain from 0.5 to 3 per cent. of vanillin, together with various resins, fatty oil, sugar, etc., etc.

The tins in which vanillas are packed should be hermetically sealed by soldering them. Each bundle should be wrapped in a sheet of tin foil, sufficiently thick to preserve them from moisture. If they are kept in too warm a place, the aroma is weakened, whilst excess of moisture causes vanilla to mould and take on an unpleasant odour which cannot be got rid of.

Mexico was the first country to produce vanilla beans, and it is only sixty years ago since they were first produced in Réunion, and later still in Ceylon, Java, and other districts where their cultivation now takes place.

There are several varieties of Mexican vanillas, the ordinary long beans, obtained by the cultivation" of *V. planifolia* being the usual high-grade Mexican beans. They are about 5 to 8 inches long, sometimes even 10 inches, and about \( \frac{1}{2} \) inch wide, striated, curved at their ends, sticky, and deep brown in colour. These are the high-grade, frosted beans.

Occasionally one meets with the wild fruits, naturally fertilised, which are shorter, and are obtained from the same plant as the former, but in its wild condition. The colour is paler and the pod is drier and does not possess nearly so strong an odour as the cultivated bean. These beans do not “frost” or crystallise. Vanillons, or pompon-vanilla, are large pods obtained from *V. pompona*. They are not nearly so delicate in aroma as the other beans; their odour rather resembles a mixture of vanilla, balsam of Peru, and Tonquin beans. The beans reach a length of 4 to 6 inches, are somewhat thin, and are soft, brown, and sticky and somewhat reticulated and mixed with over-ripe empty pods.

Bourbon vanillas, although shorter than the best Mexicans and more reticulated, yield quite as good results from the perfumery point of view. Adulteration of vanillas consists chiefly in the admixture of inferior beans with those of a better quality, or of treatment of diseased beans with balsam of Peru. The perfume and the sticky feel of such beans easily indicate such an admixture. The most inexperienced user ought to be able to recognise by their appearance beans exhausted by alcohol and which are fraudulently “reconditioned.”

Vanilla is used in perfumery in the form of alcoholic tinctures. Unfortunately, these tinctures, which are most useful when used in small quantities, are so deeply coloured by the pigment of the
beans, that they must be used with discretion. This is not the case with artificial vanillin, which is colourless, and can be used for any type of cosmetic preparation.

**VARIOUS SUBSTANCES FREQUENTLY USED IN PERFUMERY**

It is only necessary to refer briefly to a number of other substances, mineral and organic, natural or artificial, which are of some importance in perfumery, although they are not part of the perfume properly so called, nor of the actual soap or essence in which they are used. The following bodies include a few which may be regarded as colouring matters.

**Talc or Steatite.**—This substance is essentially a silicate of magnesium, a mineral matter occurring in laminated masses, varying in colour from a greyish-green to a pure white. It is found in the Alpine regions, especially in the Tyrolean Alps, in the Southern districts. It has a specific gravity of 2.74. The fragments are micaceous, almost transparent, and of a somewhat greasy nature to the touch. When finely powdered, it is, in the best qualities, pure white and soft and non-gritty to the touch. This is the quality which is used in perfumery, not only for the preparation of face enamels, etc., but as an addition to soaps and various powders, pomades and cosmetics. Faintly perfumed talc is the powder sold as "glove powder." In all cases the finest and whitest powder is necessary, and where rouges and enamels are concerned, very special qualities are required, which will be referred to later.

**Lead Carbonate.**—The perfumer is warned against the use of lead carbonate, or white lead, since it is a strong poison and should never be employed in perfumery. Its virtues, without its poisonous properties, may be supplied by bismuth subnitrate.

**Bismuth Subnitrate or Enamel White.**—This substance is a basic nitrate of bismuth combined with water. It forms a light, white powder, without odour or taste, practically without any crystalline form at all. When heated to 100°, as is usual when required for perfumery purposes, it loses all trace of crystalline structure and becomes an impalpable powder. It is still further improved by lixiviation by water, when all coarse particles are removed. It is somewhat expensive, which is the only reason that a substitute for it is sometimes sought. Amongst the
substitutes for this substance, which are not toxic, like white lead, is zinc oxide.

Zinc Oxide.—This substance, of the formula ZnO, is of a whiteness which leaves little to be desired, and it is not particularly toxic. Further, it does not blacken under the influence of sulphuric hydrogen, which is given off on burning ordinary lighting gas, which causes discoloration with both white lead and bismuth subnitrate. As will be seen later, it is not wise that face enamels and similar preparations should be used except where necessary, for example, 'in the theatrical profession. The property of not blackening under the influence of burning gas has, for this purpose, caused zinc oxide to be duly appreciated by manufacturers of this class of compound. This is also true of barium sulphate.

Barium Sulphate, or "Blanc-fisé."—This substance has the formula BaSO₄. It is quite harmless when pure and washed free from barium chloride, which is poisonous. It is a good white powder, not quite so good as zinc white, but perfectly stable and unalterable chemically. Calcium carbonate, more or less pure, forms the basis of the cheaper face enamels, and, being quite harmless, enters also into the composition of tooth powders and similar preparations. For such preparations, it must be in the finest state of subdivision, which is usually attained by careful levigation.

Silver Nitrate (caustic).—This substance, AgNO₃, has never been effectively replaced as a dye for white or grey hair. It is, therefore used as a disguise, and although its use is not recommended, it should be noted that pure silver nitrate, prepared by dissolving metallic silver in nitric acid and recrystallising the nitrate so obtained, is frequently adulterated, especially when in the form of sticks, which are obtained by pouring the melted salt into appropriate moulds. To this form of nitrate of silver, nitrate of potassium is frequently added, sometimes legitimately, when it is described as "mitigated caustic," and sometimes fraudulently without such description. The fracture of pure silver nitrate is crystalline, but with even small quantities of potassium nitrate, the fracture is conchoidal. When pure, it is very easily soluble in water, but very slightly soluble in ether, except when alcohol is added, when its solubility is increased. It dissolves in ammonia without coloration or precipitate. Its aqueous solution is neutral to litmus. A 10 per cent. solution in water should not become turbid when mixed with four times its volume of dilute
sulphuric acid, even at the boiling point. And if such a solution be treated with excess of hydrochloric acid, all the silver is precipitated and the filtrate should leave no residue on evaporation. The mere presence of organic matter (dust, etc.) will not darken nitrate of silver, except in the presence of light, when reduction will take place with consequent blackening.

To preserve the stucks of silver nitrate they must be wrapped in non-transparent black paper, or stored in dark blue or amber bottles. If allowed to come into contact with the skin, silver nitrate causes a dark stain, which is deeper according to the dampness of the band. If the stains are moistened with a solution of potassium iodide, and then, in a few moments, washed with water, they will be removed.

**Glacial Acetic Acid.**—This acid has the formula C₂H₄O₂, and is used to some extent in perfumery. Being of an antiseptic nature, and capable of dissolving most essential oils to some extent, it is a useful base for the preparation of toilet vinegars and acid smelling salts. But it should be of the purest quality and be quite free from empyreumatic matter, which is present in many commercial samples. It is a colourless liquid, of characteristic odour and taste. When it is of 100 per cent. strength it solidifies between +5° and +10° into a crystalline mass, and melts at +16°. Its specific gravity varies according to its actual strength. At 100 per cent. it is 1-060, whilst when weaker, it will increase to 1-070. At about 50 per cent. strength its specific gravity is again 1-060. So that its strength cannot be determined except by analysis. Acid of 84 per cent. strength will dissolve 1 per cent. of lemon oil without turbidity, which is not the case with weaker acids. If the acid be saturated with sodium carbonate, empyreumatic matter can at once be detected by its odour. If 1 volume of the acid be diluted with 2 volumes of water, and a few drops of solution of potassium permanganate are added, the latter will rapidly be decolorised if empyreumatic matter be present.

**Acetic Ether.**—Acetic ether, CH₃CO₂CH₃, is a clear, colourless, volatile liquid, of a refreshing odour, recalling that of acetic acid, but much more fruity. Its specific gravity is 0.900 to 0.904. It boils at 74-76°. It is slightly soluble in water, and soluble in all proportions in alcohol. This ether liberates free acetic acid under the influence of sunlight; to render it neutral again, it should be shaken with sodium bicarbonate and filtered.

**Phenol.**—This acid body is derived from coal tar and has the,
formula \( C_6H_5O \). It is a powerful antiseptic and is sometimes used as such in the manufacture of antiseptic washes and toothpastes. The substance used is, of course, the pure acid, which crystallises at the ordinary temperature in long needles. It is colourless, and has a burning taste and a strong penetrating odour, which is not, however, very lasting. Its melting point varies according to its degree of purity, and when melted it forms an inflammable liquid. It is soluble in water, but more so in alcohol, ether, and glacial acetic acid.

**Starch.**—This important raw material is a carbohydrate of the empirical formula \( C_{6n}H_{10n}O_n \), and is met with in nearly every portion of most vegetable tissues. Commercially, it is extracted from wheat, maize, potato, and the roots of numerous tropical plants, such as arrowroot. Rice starch is the most usual variety employed in perfumery. Wheat starch as met with in commerce is usually too lumpy for use in perfumery—that is, for the preparation of toilet powders. It must be ground to a very fine powder before being used. Rice starch is nearly identical with wheat starch (except that it is, perhaps, not quite so adherent to the skin). Perfumers usually employ only these two varieties, and seldom use potato starch, which is too dense and impure, and lacks that special whiteness which characterises powders prepared with rice and wheat starch. Starch "cracks" by the pressure of the hand. If it lacks this character, it is certain that it contains excess of moisture. To get it into condition, it must be completely dried by artificial heat. A good quality pure starch should not contain more than about 15 per cent. of its weight of moisture. Mineral adulterants are detected by incinerating the starch, and examining the ash in the usual manner.

**Glycerine.**—Glycerine, \( C_3H_5(OH)_3 \), when in the purest condition in which it can be obtained, is a colourless, odourless, syrupy liquid of specific gravity 1:260. It is soluble in all proportions in water and alcohol, but insoluble in chloroform, petroleum ether, and fatty oils. It is very hygroscopic and will absorb 50 per cent. of its weight of water from the atmosphere. Its boiling point is about 290°. It is, however, carried over by a current of steam, in quantities depending on the pressure of the steam. Heated considerably above its boiling point, it decomposes and gives off acrid vapours of acrolein. Neither sulphuric acid nor aqueous alkalies in the cold effect any alteration in its character. Glycerine is prepared by the saponification of fatty bodies. The best quality results from saponification by superheated steam.
The aqueous solutions of glycerine, freed from suspended fatty acids, are evaporated, either at normal pressure, or in vacuo. The crude glycerine is purified by vacuum distillation. It is unfermentable, and practically anhydrous when of specific gravity 1.260. But when pure it has a tendency to irritate the skin, on account of its hygroscopic properties. When diluted with 40 to 50 per cent. of water it ceases to be hygroscopic. When heated with dilute sulphuric acid, it should not evolve any odour of butyric acid. Impurities such as lime or sulphuric acid are detected by the usual analytical tests. Glycerine reduces silver nitrate, chromic acid, and bichromate and permanganate of potash, and should not therefore be used in connection with these bodies.

**COLOURING MATERIALS**

The principal colouring matters used in perfumery are blue, yellow, black, brown, red, green, and violet.

Indigo is the only natural blue colour which is used, and it is employed in the following manner: 20 grams of finely powdered indigo are dissolved in 200 grams of sulphuric acid (65 per cent.) in a glass vessel, until effervescence has ceased. The product, known as Saxe blue, must be neutralised by adding calcium carbonate until no further evolution of gas takes place, when the mixture is allowed to stand and is then filtered. To the liquid colour so obtained, 25 per cent. of alcohol is added in order to preserve it. An indigo paste, already prepared, can be purchased, which, on dissolving in 80 parts of water, yields a powerful colouring matter, ready for use. Such a solution gives a good blue colour to 1000 times its volume of liquid.

Prussian blue, and the various synthetic blues, such as methylene-blue, are not recommended for use in perfumery on account of their possibly toxic effects.

There are numerous yellow colours used in perfumery. One of the most stable is that from saffron, *Crocus sativus*. This is reduced to a form suitable for colouring purposes by boiling 200 grams of saffron in 500 c.c. of water, and decanting the yellow liquid; the residue is again boiled with 1000 c.c. of water and to the united aqueous extracts are added 100 c.c. of alcohol. The residue from the aqueous extracts is then treated with 900 c.c. of alcohol and the alcoholic extract is mixed with the aqueous extracts previously obtained; the mixture is a rich
yellow ready for use, so that 1 part gives a good yellow colour to 1000 parts of colourless material.

Carthamus tinctoria, sometimes known as bastard saffron, gives a good yellow colour when extracted by alcohol, but as it has a powerful purgative action, it is not usually employed in perfumery; the objection is, of course, purely sentimental. The use of aloes, which gives a fine yellow colour, is in the same category. Turmeric (Curciima tinctoria) gives a good yellow solution, which is not very stable towards sunlight. Its taste and odour are also against its general employment. Fustic (Rhizs cotinus) yields a fine orange-yellow colour, changed by alkalies to a purple-red. It is, however, somewhat toxic and must be used with care. Bixine is sometimes, but not often, used to colour oils, both fatty and hydrocarbon. Quercitrin, from quercitrin wood, gives a golden-yellow with alkalies and a greenish-yellow with acids. It can only be used externally. Synthetic coal-tar yellow need not be discussed here.

Caramel.—This product is largely employed in perfumery, usually in alcoholic solution, and also in fine soap manufacture. It can be used to give a colour varying from amber-yellow to deep brown. Mixed with indigo or with chlorophyll, it gives all shades of green, from an olive to a "dead-leaf" green. Mixed with saffron and indigo carmine, it gives the lighter shades of apple-green. When pure, caramel, if used with discretion, is of great value in perfumery colouring. It is a thick, syrupy, brown liquid, obtained by heating crude cane— or beet—sugar, or glucose, which has been obtained by the hydrolysis of starch, to a high temperature, usually with the addition of a little caustic soda. It is a viscous liquid, which is semi—solid on cooling to a low temperature, unless a small quantity of water is added so as to keep it in a liquid condition. Caramel has a powerful colouring capacity, and is absolutely innocuous. It is advisable, however, to use a caramel prepared with sufficient care to ensure freedom from traces of arsenic, which may be present when it is manufactured from glucose with impure sulphuric acid.

Black Colours.—These colours are hardly ever used except for the preparation of eyebrow pencils and certain other cosmetic preparations. Pure charcoal or ivory black in the solid form, or "Chinese Ink" in the liquid form, are practically the only varieties employed. Brown colours are obtained by mixing yellows with caramel, or with alcoholic extracts of gum benzoin,
NATURAL RAW MATERIALS USED

tolu, or storax—of sometimes with metathenylenediamine, which is toxic and should never be used. Mineral colours of the iron oxide type are used to a small extent as brown colouring matters.

Red Colours. —Red colouring material is principally employed for powders, pastes, soaps, and liquid dentifrices, enamels, creams, and rice powders. The principal material used is cochineal, and its active principle carmine. A mixture of cochineal is used to colour liquid dentifrices, and is prepared as follows:

- Powdered cochineal ............ 1 part.
- 80 per cent. alcohol ............ 10 parts.

The mixture is macerated in a closed vessel for ten days with occasional shaking, and is then decanted, the mass pressed, and the liquid filtered. The exact shade of red can be modified by suitable additions. A golden-red results from the addition of a little tincture of benzoin, an orange-red by the addition of a little citric acid; a violet-red by a little caustic alkali or a small quantity of indigo carmine. Trial mixtures will rapidly give the desired quantities for any given shade. Powdered carmine is usually used to colour powders and tooth-pastes. For powders, the quantity varies from 0.25 to 1 per cent., and for pastes and creams from 1 to 2 per cent. If the slightly violet shade needs correction, a little eosin can be added. Carmine is prepared by treating powdered cochineal by sodium carbonate and alum, or similar mixtures, and extracting by well-recognised chemical processes. A good "liquid carmine" is given by the following formula:

- Powdered cochineal ............ 10 grams.
- Powdered alum ............ 25 g.
- Cream of tartar ............ 25 g.
- Distilled water ............ 150 g.

The water is heated to boiling point, and the cochineal added; after five or six minutes' boiling the alum and the cream of tartar are added, the whole is well stirred, and allowed to cool. The filtered liquid gives the base for numerous shades, from pale to the most intense red.

Red sandalwood, or red Sanders wood, is used as a tincture, prepared by macerating 1 part of the powdered wood with 5 parts of 80 per cent. alcohol. For colouring liquid dentifrices, use 3 per cent. of this tincture. The colour is very stable.

Logwood, which contains hæmatin, gives a good red colour.
but it is not very soluble in water. Dilute acids turn it a yellow, and alkalis a purple-red colour. It must be prepared in a perfectly neutral condition, and with strong alcohol as the solvent. Haematin can also be purchased already prepared. To extract the haematin, the powdered wood is triturated with ammonia, and the pasty mass exposed to the air until the smell of ammonia has dissipated; oxidation then proceeds and the oxidised haematin can be dissolved out as a colouring agent.

The extract from Archusa root furnishes a red colouring matter which is soluble in alcohol, fatty oils, hydrocarbon oils, etc. This colour can therefore be employed for oils, pomades, etc., and furnishes shades varying between pale rose and deep purple. One hundred grams of the powdered root are moistened with 10 c.c. of distilled water containing 1 gram of citric acid. The mixture is allowed to stand for several hours, and then 80 per cent. alcohol is added. In eight days, the mixture is filtered and the liquid is then ready for use. Alkanin, the colour-principle of anchusa, can be obtained commercially.

Orchil is a colouring matter extracted from Roccella tinctoria, and is principally employed in colouring alkaline hair lotions. The red shade is deepened by acids and turned to a violet-red by alkalis.

The extract from Bixa orellana contains several colouring matters, both yellow and red. The principal of these is a red colour known as bixin. It is used in alcoholic solution to give golden-red effects.

Synthetic reds are remarkable for the wide variety of shades obtainable. These are generally less expensive than the natural colours, and require very simple preparation. They only require to be dissolved in water, or in a mixture of water and alcohol, to the strength of, say, 1 per cent., and they are then ready for use. One c.c. of such a solution is usually sufficient to colour a large volume of liquid. It is, however, necessary to take into account the chemical properties of the colour, especially its behaviour towards acids and alkalis. Two principal classes of these colours exist, the basic colours and the acid colours. Basic colours are usually precipitated by tannic acid, whilst acid colours are not. The manufacturer of such colours usually describes his colours in this respect, so that the user knows what he has to deal with.

Synthetic reds are so numerous that it is impossible here to enumerate them. Eosines, erythrosines, Bengal red, Bordeaux red, fuchsines, and others are amongst the most generally used
varieties. The cosines, of which there are many shades, give an exceedingly fine “rose-eglantine” shade. It is fairly resistant to light and to acids. In alcoholic solution, cosine is fluorescent, giving a green colour with reflected light. By using the potassium compound, this fluorescence is obviated.

Green colours are usually obtained by mixing blue and yellow shades, frequently, however, chlorophyll, the natural colouring matter of plants, is employed to colour liquids green. Saffron-yellow and indigo furnish good green shades; such as apple-green and “vert pré.” Indigo and caramel give olive-green and “dead leaf” green. Chlorophyll-green is of a very fine shade. It is, however, easily decomposed by light, and has a tendency to form deposits unless the amount of alcohol present is sufficient to keep it in solution. The plants employed for the preparation of chlorophyll are spinach, nettles, lemon-grass, etc.

It can be obtained by boiling the leaves with alcohol, pressing the mass, filtering the liquid, and recovering the alcohol, or by using the substance in the alcoholic solution. Guillemare and Lecourt treat spinach leaves with a weak solution of soda. This dissolves out the chlorophyll, and the excess of soda is neutralised with acid, leaving a neutral solution of the chlorophyll.

It is often, however, desirable to purchase the colour just in the form in which one wishes to use it, and one can purchase such colours of all shades and concentrations, relying on the quality being of the best, and so avoiding all risks of one’s own unskilled manufacture.

A synthetic green, known as malachite green, is useful for some purposes, but its colour is fugitive in the presence of alkalies. Various artificial greens can be obtained which are not affected by light.

Violet colours are obtained by mixing reds with blues. They are, however, not often employed except for lilac extracts. A synthetic lilac can also be used for this purpose.