CHAPTER 10

ÉTHAL[1]

§1. COMPOSITION

479.

	BY WEIGHT		BY VOLUME[2]
Oxygen………………	6.2888	100.00	1.00
Carbon………………	79.7660	1268.40	16.60
Hydrogen……………	13.9452	221.74	35.54

which is equivalent to:

Ethylene……..	92.925	100	16.6	16.6 carbon 33.2 hydrogen
Water………..	7.075	7.61	2.00	1 oxygen 2 hydrogen

480. The composition of cetyl alcohol is remarkable not only because it can be represented by ethylene plus water but also because the ratio between those two components appears to be in a simple relationship with the ratios between ethylene and water in the compositions of alcohol and ether[3]. In fact, 100 parts by weight of ethylene are combined with 63.23 parts of water in alcohol, with 31.61 parts in ether and with 7.61 parts in cetyl alcohol, and these proportions are near enough 8 : 4 : 1.

§ 2. PHYSICAL PROPERTIES

481. It is colorless and has the semi-transparency of wax; at ambient temperatures, it is a solid. When it is melted in water, a thermometer inserted into the mixture will read 50°C and this will rise to 51.5°C as the mixture solidifies, but when cetyl alcohol is melted in the absence of water, the thermometer shows 48°C[4] when crystals are being formed. When cooled slowly, cetyl alcohol crystallizes in small shiny flakes and occasionally, radiating needles can be observed on the surface. It volatilizes at a temperature that is markedly lower than that necessary to volatilize non-acid fatty matter; this can be demonstrated by saponifying spermaceti with potassium hydroxide in a porcelain dish above which a glass funnel has been positioned. When the temperature is raised to the boiling point of the liquid, the walls of the funnel become covered with a

white substance which is cetyl alcohol. Finally, by heating the cetyl alcohol on a sand bath in a small dish, it can be volatilized in its entirety.

482. Cetyl alcohol is odorless or almost odorless and tasteless.

§ 3 CHEMICAL PROPERTIES THAT ARE OBSERVED WITHOUT THE CETYL ALCOHOL BEING ALTERED

483. Alcohol with a density of 0.812 (g/mL) is completely miscible with it at a temperature of 54°C. When the cetyl alcohol slowly precipitates from the solution, it crystallizes in small flakes that are shiny but less so than spermaceti. In solution it has no effect on blue litmus, nor on red litmus or on hematin, not even when so much water is added[5] that the cetyl alcohol does not precipitate.

484. It does not release any water when heated with lead oxide.

485. When cetyl alcohol is immersed in cold water, it does not dissolve. The only noticeable effect is that it becomes slightly white at the surface, which is probably caused by some interstitial water. If the material is taken out of the liquid and exposed to the sun, it regains its original appearance and does not release any trace of water vapor when it is melted in a glass tube that is closed at one end.

486. When cetyl alcohol is heated in pure water or in alkaline water, it undergoes no change whatsoever. Frequent washing of cetyl alcohol that has been heated in alkaline water shows this to be absolutely free of potassium, from which it follows that cetyl alcohol is not able to combine with this base.

487. Although the effect of aqueous potassium hydroxide on pure cetyl alcohol is nil, this is not the case when *cetyl alcohol is combined with a very small amount of a combination of palmitic acid and oleic acid with a melting point of about 20*°C: I was able to observe this in the following circumstances. I took some cetyl alcohol that had retained a small amount of palmitic acid and oleic acid and allowed it to react with water containing its weight in potassium hydroxide. In the end I obtained a *flexible, soapy material that was lightly citrine-colored* and that melted between 64 and 60°C, after having exuded the alkaline water in which it had been allowed to react. I will now describe the properties of what I have called *flexible, soapy material.*

488. An amount of 0.500 g of *flexible, soapy material* that had been washed with water, pressed vigorously between paper and then melted, was then treated with hydrochloric acid. This led to the formation of

Flexible soapy material

47 mg of potassium chloride, which corresponds to 29.7 mg of potassium oxide, and 0.400 g of cetyl alcohol combined with a small amount of palmitic and oleic acid. This cetyl alcohol melted at 50°C[6]. Thus:

Cetyl alcohol..	400	100
Potassium oxide.......................................	30	7.5

489. An amount of 0.500 g of *flexible soapy material* mixed with 20 g of water lost its semi-transparency and its light citrine color. On absorbing the liquid, it became milky white. After a contact time of three hours, it was brought to the boil and formed a perfect emulsion. After having been concentrated to half its volume, the surface was covered with yellowish droplets of an oily appearance that congealed on cooling, absorbed water and formed a thick, white, mucilaginous liquid. This liquid was diluted with a large amount of water and poured into a filter in which the insoluble material was washed until the washing water had no more effect on hematin.

Washing water

490. The washing water contained a small quantity of palmitic acid and oleic acid soaps but the quantity was so small that no fatty acid droplets could be obtained when hydrochloric acid was added to the concentrated washing water.

Washed material

491. The washed material resembled aluminum hydroxide gel. When heated gently in a small platinum dish, it changed into a milky, fluid liquid that was soon covered with yellow oily drops. When the material was removed from the fire, it set into an opaque mucilage on cooling. Finally, when all the water had been removed from the mucilage, the resulting material, when molten, resembled a yellow oil; it consisted of:

Fatty material that is slightly acid to litmus......	100
Potassium oxide...	0.63

492. Therefore it follows: 1. that the water has removed a large part of the potassium and a small amount of the palmitic and oleic acids from the *flexible soapy material*; 2. that the *washed material* was still able to form a mucilage with water although it contained only a very small amount of potassium.

493. If the *washed material* is treated with hydrochloric acid to remove all traces of alkalinity, a substance is obtained that does not form a mucilage with water; it just turns white. But as soon as a few drops of potassium hydroxide are added, the mucilage is produced instantaneously. If the alkali is in excess, the mucilage is not homogeneous. It is lumpy because the alkali is too strong and cannot interpose itself as well as when it is weak. This effect is analogous to that shown by an alkaline

solution, which fails to dissolve soap when it has reached a certain concentration.

494. It goes without saying that after neutralization of the palmitic and oleic acids that are combined with the cetyl alcohol by baryta water, perfectly pure cetyl alcohol can be obtained by treating the dried residue with alcohol of a density of 0.791 (g/mL[7]).

495 When 60 parts of a mixture of palmitic and oleic acids with a melting point of 45°C are combined with 40 parts of cetyl alcohol, a compound[8] is formed that has a melting point of 43 to 44°C.

§ 4. CHEMICAL PROPERTIES THAT ARE OBSERVED WHEN THE CETYL ALCOHOL IS ALTERED

496. When cetyl alcohol is heated sufficiently in contact with air, it burns like wax.

497. An amount of 0.2 g cetyl alcohol was put in a glass tube with an internal diameter of 0.01 m together with 2 grams of sulfuric acid at a temperature of 18°C. After a contact time of five minutes, the cetyl alcohol was still white. After two hours, it was slightly red[9] and hardly any or no sulfur dioxide evolved. The acid did not change color either. After twenty-four hours, the cetyl alcohol showed signs of softening and the acid was slightly citrine colored. After a week, the cetyl alcohol had not dissolved. It formed a solid layer on top of the acid and was white with a tinge of red. The parts of the layer that are in contact with the acid had a purple color. No sulfur dioxide could be demonstrated with litmus paper. The sulfuric acid was citrine colored and slightly opaque in the layer touching the cetyl alcohol.

Effect of sulfuric acid of 66 degree on cetyl alcohol while in contact with air

498. At 100°C, the cetyl alcohol is molten and turns a strong reddish brown color. Sulfur dioxide is released. The largest part of the cetyl alcohol remains undissolved and the sulfuric acid is only very slightly colored. In this respect, the cetyl alcohol behaves quite differently from stearic acid, oleic acid, stearin and olein.

499. At a temperature above 100°C, the cetyl alcohol darkens without mixing into the sulfuric acid. Some sulfur dioxide gas is evolved which I think is mixed with hydrogen sulfide.

500. At ambient temperature, 2 grams of cetyl alcohol and 200 g nitric acid with a reading of 32° on a hydrometer do not react. If the reagents are heated, it becomes clear after one hour that a large amount of nitrous acid has been formed. After proceeding as explained earlier (46), a

Effect of nitric acid

residue of 1.735 g is obtained that is almost colorless, acid and partially crystallized; this residue is then separated into an *aqueous extract* A and an *alcoholic extract* B.

A. Aqueous extract

501. It yields *acid crystals* and a mother liquor that is only slightly yellow. It is not astringent and it does not form a precipitate with lime water.

Acid crystals

502. They are similar to the *acid crystals* prepared from stearic acid (48).

B. Alcoholic extract

503. When evaporated to dryness, it leaves a residue of 85 mg. When this is dissolved in alcohol and the alcoholic solution is mixed with water, a very small amount of *oil* is obtained together with an *aqueous liquid*.

Oil

504. It has a slightly bitter taste and to me it seems similar to the oil from stearic acid (51). It acts like the latter on litmus paper.

Aqueous liquid

505. It contains the same substances as extract A.

Some observations on cetyl alcohol

506. When comparing alcohol, ether and cetyl alcohol with each other, it is clear that the fatty character of these compounds becomes less pronounced, the more water they contain[10]. Accordingly, cetyl alcohol is totally insoluble in water. It is volatile like a kind of wax and highly flammable. Diethyl ether, with its slight solubility in water, is a step further away from oils and fats. Finally alcohol, which is less flammable than ether, is miscible with water in all proportions. Moreover, it is remarkable that by doing so, it loses its affinity for fatty materials which it dissolves in large amounts when it is dephlegmated[11] and at the same time becomes capable of dissolving substances that are very soluble in water such as sugars, on which it has no effect or very little in the concentrated state.

§ 5. PREPARATION

507. (See Book III, Chapter 2.)

§ 6. NOMENCLATURE

508. I have coined the name *éthal* from the two first syllables of the words *ether* and *alcohol* because of the similarity of the composition of these three compounds.

§ 7. HISTORY

509. The first time that I mentioned *éthal* (cetyl alcohol) was during an oral presentation at the Academy on 26 February 1818.

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[1] As will be mentioned in sub-section (508), the author has coined the name *éthal* himself. In this translation, the current name *cetyl alcohol* will be used from now onwards.

[2] The molecular formula of cetyl alcohol (1-hexadecanol) is $CH_3(CH_2)_{14}CH_2OH$ or $C_{16}H_{34}O$ so the analytical data reported by the author are quite accurate.

[3] Looking for simple relationships is fully in accordance with Dalton's law of definite proportions: When two elements combine to form more than one compound, the amounts of one of them which combines with a fixed amount of the other exhibit a simple multiple relation.

[4] According to the *Handbook of Chemistry & Physics*, the melting point of 1-hexadecanol is 49.3°C.

[5] When studying potassium butyrate (368), the author noted that the presence of water could affect the coloration of litmus paper, so it is only logical that he investigated this aspect.

[6] Previously, the author reported a solidification point of 48°C. Perhaps, the sample was contaminated with some fatty acids which the treatment with potassium hydroxide removed. After all, there is a substantial weight loss.

[7] This is absolute alcohol.

[8] This is not a true compound in the chemical sense. It looks more like a eutectic mixture.

[9] The French word 'roux' can mean: red, auburn, ginger, russet and reddish brown.

[10] This refers to sub-section (480) where it was shown that a given weight of ethylene in alcohol (ethanol) contains 8 times as much water as the same weight of ethylene in cetyl alcohol and that the same weight of ethylene in diethyl ether contains 4 times as much water. Perhaps an easier way to arrive at Dalton's law would be to express the ethylene contents per fixed amount of water. This also leads to a ratio of 8 : 2 : 1.

[11] To *dephlegmate* means to remove water from something. Consequently, dephlegmated alcohol will be absolute alcohol. It was prepared for the first time in 1796 by Johann Tobias Lowitz (1757-1804).