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Wax Acids and Emulsifiers from Products
of the Synthesis of Hydrocarbons from
Water Gas, and Their Utilization
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The primary products of the synthesis process are known to be suited in very special manner as raw materials for future chemical conversion 1) 2). Here may be mentioned the polymerization of unsaturated gas oils to valuable naphtha, or their conversion into alcohols, furthermore the aromatization of individual naphtha fractions, polymerization of unsaturated naphtha to lubricating oil and catalytic cracking and reforming, especially of gas oil, for the production of high octane gasoline. All these reactions are favored by the uniformity of the primary products and their extraordinarily small content of sulfur and resinous material.

To these reactions which already have been at least partially carried out in large scale operations, belongs also the catalytic oxidation of paraffin scale with air 3), 4) and 5) from which result as the main product, high molecular fatty acids in the soap fatty acid region. By paraffin scale is meant the fraction of the primary product boiling above the gas oil range and having an end point of around 450°. In a normal pressure synthesis it occurs as a residue in the fractionation of the condensate oil, while in medium pressure synthesis it must be separated from the hard paraffin fractions by means of a special vacuum distillation. The fatty acids resulting from this oxidation owe their suitability for use particularly to the favorable long extended straight chain form and to the uniformity of the paraffin. Uniformity here is equivalent to the complete absence of cyclic hydrocarbons, approximate absence of branched paraffins and very slight content of olefins which disturb the oxidation. The structure briefly described for paraffin scale is also valid for the high melting paraffins, that is, the plate paraffins with a melting point of around 50° and the hard paraffins with a hardening point of around 90°. Both products represent valuable initial materials for the industries which refine and use paraffins and waxes, since they differ from natural paraffins by quite characteristic properties; for example, the plate paraffin is particularly odorless, while the hard paraffin is distinguished, in addition to its heretofore unattained melting point, by a hardness which is extraordinary for a paraffin;

here by hardness is meant not melting point but the true hardness, that is, tensile or notch strength which, in general, is measured by a penetrometer 6) and is also reported as penetration number. It is this property particularly which brings the hard paraffin into close relationship to some natural waxes. The refined hard paraffin is, therefore, also designated as hard wax which to be sure does not agree with the common definition of waxes but seems justified because of its properties. The cause for this wax-like behaviour is probably to be sought in the high mean molecular weight which with a hardening point of 90° lies at around 600-650 corresponding to $C_{40}-C_{45}$, although the crystalline structure peculiar to paraffins is naturally not entirely surpassed and thereby a certain difference from natural waxes results since natural waxes have a microcrystalline structure.

In the wax and paraffin industries today paraffins with melting points of $50-70^{\circ}$ are frequently designated as hard paraffins 7) and for designation of synthetic paraffins we must use some expression such as extra hard or super hard paraffins. Instead of these I should like to propose the designation "hard paraffin" for the paraffins melting above 80° which, according to the work of Pichler 8), can go as high as melting points of 130° and to give the paraffins melting from $50-80^{\circ}$ a designation such as, for example, "middle paraffins" so far as special terms are not customary, as for example, plate paraffin 50-52 etc. By this distinction an essentially clearer separation of the types of paraffins is obtained while the question may still be left open as to the place in this scheme for inserting the term ceresin, for which a more accurate definition also would be highly desirable. Recently some work has been done on this at another place 9).

The previously mentioned physical relationship with the waxes caused us to examine whether it was not possible, by way of chemical treatment, to increase the wax-like properties of synthesis paraffins so that compounds chemically related to the true waxes should be prepared. Air oxidation 10) produced such a profusion of oxidation products like acids, esters, alcohols, ketones, etc. that it was not possible to arrive at individually defined compounds. It has been possible, however, by other means and using agents which give off oxygen to obtain almost pure wax acids. Thereby we were able also to prepare emulsified agents with quite special properties and the wax alcohols are available to us so that we can advance the true chemistry of waxes.

At this point perhaps a brief indication is desirable for better understanding of natural waxes 11), their properties

and composition. As waxes are designated the solid or liquid natural products which are mainly esters of high molecular fatty acids--the wax acids--with high molecular alcohols--the wax alcohols. Waxes can be classified according to various principles, for example, we may distinguish solid or liquid waxes, animal or vegetable waxes and also hard and soft waxes. The best known natural waxes are: beeswax, carnauba wax, candelilla wax, wool wax, spermaceti, montan wax.

The utilization of waxes is influenced by their physical properties, which are again for the most part dependent upon their chemical composition. Three main fields of application can be distinguished: (1) surface protection, (2) emulsion formation or improvement and (3) regulation of the consistency of pastes and salves. The suitability for surface protection can be derived from the origin of some waxes, for example, in the case of carnauba wax which, of course, in nature is a coating on the leaves of a palm tree and is used industrially for like properties. Particularly characteristic examples for use 2 are wool wax which is known in its purified form as lanolin and for use 3 beeswax which also acts as emulsion improver.

Certain common characteristics can be noted in the properties of the waxes; these are a conchoidal fracture, micro-crystalline almost amorphous structure and as particularly important technological property, plasticity which, of course, lies far below the melting point.

Concerning the chemical composition of waxes the following can be said: they are, as already mentioned, predominantly esters like the fats but differ essentially from the fats through the fact that they contain no glycerine and that they are resorbable. They are also appreciably more complex in structure, that is, they contain free acids, alcohols and hydrocarbons whereby the purification of the fatty acids or rather wax acids, which has more than scientific interest, is made much more difficult. The composition of beeswax and carnauba wax, for example, is the following: beeswax is principally the melissyl ester of palmitic acid and free cerotic acid in a proportion of 86:14 but it also contains free melissic acid, free melissyl alcohol and ceryl alcohol and round 12% paraffin hydrocarbon, beside various other substances in smaller amounts; carnauba wax consists mainly of the myristic acid of cerotic acid and, in addition, contains free cerotic acid, carnaubic acid, ceryl alcohol, myristic acid, melissyl alcohol and small amounts of hydrocarbons.

The acids mentioned are "chemically speaking"
saturated fatty acids and thus are homologues of the soap
fatty acids. By "high molecular fatty acids" at present is

generally understood in the industry soap fatty acids, that is, acids which lie in the molecular range of around C_{12} - C_{18} and which are suitable for the manufacture of soaps. Before paraffin oxidation was carried out technically, they were obtained only by the splitting of natural fats, for example, from tallow, palm oils and other fats and oils.

The counterpart of the soap fatty acids in the molecular range above C_{20} are the wax acids 12). The most important which are contained in natural products are: lignoceric acid, carnaubic acid, cerotic acid, carboceric acid, montanic acid, melissic acid, myristic acid, to which the corresponding alcohols belong carnaubyl alcohol, ceryl alcohol, montanyl alcohol, melissyl alcohol and myricyl alcohol. The assignment of carbon numbers to the individual acids is not entirely clear, for example, for montanic acid C_{28} and C_{29} , for C_{24} both carnaubic and lignoceric acids are assigned. These confusions occur as a result of high molecular weight and the long hydrocarbon chain, since not all reactions can be so simply carried out as, for example, in the case of the soap fatty acids. For instance, this is shown particularly unfavorably in the saponification of esters, in that the carboxyl group has only a very slight influence upon the entire molecule. The high molecular weights produce such high boiling points that even vacuum distillation of the wax esters is practically no longer possible, and that of the methyl esters is only possible in high vacuum 13). A further result of the long paraffin chain is particularly for paraffins, an increased difficulty in solubility. All these properties, together with the previously mentioned complex structure of the waxes, affect the purification of the free wax acids so greatly that, to a large extent, they have been disclosed only through the oxidizing refining with chromic acid from crude montan wax, that is, from wax acids obtained from a natural product 14). We have now been successful in preparing from synthesis paraffins, completely synthetic wax acids which also can be esterified; the esterification can then be undertaken with any desired mono- or polyvalent alcohols so that wax esters with quite different consistencies are produced. However, the higher the molecular weight, of the monovalent alcohol used, so much the harder are the esters obtained, that is, they resemble so much more closely the properties of carnauba wax.

Up to the present in a technical series of experiments we have produced two different products, wax acids 1 and 2. They differ from one another essentially in melting points, wax acid 1 has a hardening point of 80° and wax acid 2 a hardening point of 45 - 50° . Both contain about 40-50% unsaponifiable in the form of unchanged paraffin. The neutralization or acid

numbers can be adjusted accurately according to the purpose of application; in general, they are maintained between 70 and 100, the saponification numbers then are between 80 and 110; the content of unseponifiable also varies somewhat. In both products, in addition to paraffin, there are completely saturated acids since the iodine numbers are about 2-3. The color is almost white, and hardness, particularly for wax acid 1, is very high; the penetration numbers are within the range of hard paraffin at 5-10; wax acid 2 is appreciably softer and more similar to soft wax.

The aforementioned technical data will be supplemented by the properties and the composition of the pure wax acids which we prepared from wax acid 1 and studied more accurately. They are designated as wax acid 3 and are practically paraffin free. The hardening point is 90° and the neutralization number 145-150.

In the investigation which we undertook, it was found that the acids are predominantly mixtures of saturated aliphatic carboxylic acids essentially over C_{20} , having an average C number of around 25-30. The separation into individual units is extraordinarily difficult; even with the aid of vacuum distillation of the methyl esters at, for example, 0.5-1.0 Torr. it could not all be distilled, aside from the fact that naturally the boiling points of the methyl esters of the wax acids are still not known completely so that, during the distillation we were forced to choose the cuts so that as far as possible the fractions contained only two acids. So far as we are able to summarize here, about 10-15% of the acids are in the molecular range of less than C_{19} , about 45% lie less than C_{27} and 60-62% less than C_{34} . Since it is not possible to distill further than up to $280-300^{\circ}$, in the distillate with the vacuum stated only about C_{35} is reached. The melting points of the fractions, since they are a matter of mixtures, do not agree completely with those of the normal acids (15), we always found in a $C_{23}-C_{24}$ fraction a hardening point of 69° and melting point of 70° , while carnauba acid, which is primarily a C_{24} acid has a hardening point of 67-69 and a melting point of 72.5° . For the cerotic acid from beeswax a melting point of $78-79^{\circ}$ is given and a carbon number of 25, 26, or 27 while for a $C_{25}-C_{27}$ fraction we found a melting point of 76° . The acid mixtures also arrange themselves quite well in this scheme although the hardening point and the melting point for wax acid 3 at 90 and 190° respectively are very high. Apparently the highest melting fractions, as is also the case in hard waxes, have a definite influence upon the end melting point. By variation of the

reaction conditions, even higher acids can also be produced, for example, a mixture with an average of C35, whose hardening point is 105° and melting point 117°. For comparison with the wax acids prepared from crude montan wax by oxidizing refining and in comparison with refined montan wax, I should like now to give the flow and drop points of the acids.

	<u>Flow Point</u>	<u>Drop Point</u>	<u>Hardening Point</u>	<u>Melting Point</u>
Wax acid from Montan wax	81°	82°	78°	85°
Refined Montan wax	71	72	72	91
Wax acid 3				
C27-30	100	101	90	109
C35	108	109	105	117

It may be seen that here acids are present such as have never before been produced with these molecular weights, because such high molecular acids do not actually occur in nature. At present we are occupying ourselves with the separation of the acids still further by other means so far as they are above C30. Even though it is only difficultly possible to arrive at very pure individual compounds, yet the preparation of binary mixtures is sufficient to give a preliminary characterization.

By-products are contained in the wax acids only in very slight amounts, which is evidenced through the fact that the proportional number 16), that is, the proportion of ester number to acid number is extraordinarily small; it is approximately 0.07. It may probably be assumed that in our wax acids we are dealing with saturated and predominantly straight chain acids with scant content of branched compounds. This may be concluded, if one disregards the melting point, from the great hardness in combination with the small iodine number of about 2-3. By way of the wax acids the previously mentioned wax alcohols have also been rendered accessible. The reduction of the acids can be carried out in different ways and leads to products with very low acid and saponification numbers, but with high OH-numbers which are comparable with alcohols such as myrisyl or melissyl. We obtained from wax acid 3 the following alcohol: neutralization number 15, saponification number 20, OH number 140. The hardening point is 86°C, the melting point 102°.

For wax alcohols the following melting point data are recognized 17); C₂₄ alcohol 77°, C₂₆ alcohol 79°, C₂₈ alcohol 83°.

We see here also that the alcohols which we prepared come within a molecular range concerning which heretofore very little information is available. More particular details concerning this and concerning the properties of the esters, which therefore correspond to the true waxes, must be postponed for later work. Up to the present, in any case, it is shown that their properties such as plasticity, oil absorption and oil combining capacity correspond completely to natural waxes.

Starting from the wax acids we have also developed emulsifying agents which show quite characteristic properties. Perhaps also some general remarks concerning emulsions may be made here. By an emulsion is understood a system of two liquids 18) which are not miscible with each other or only slightly so, or a system of a solid substance and a liquid, in which one or both liquids or the solid substance is present in a state of very fine subdivision. The solid-liquid system is designated as a suspension but in the following, in all cases insofar as a solid liquid system is concerned, the expression emulsion is used, except for those cases in which finely divided solid bodies, such as, for example, soot or kaolin, are participants, whose emulsion-like product to a suitable degree retains the designation "suspension". In general, also there is mention of dispersions 19) wherein according to particle size we have coarse dispersions, emulsions, and colloids. Emulsions occur when the particle size 20) amounts to around 10⁻⁴cm. while colloids have particle size of about 10⁻⁵-10⁻⁷cm. Further differences between emulsions are these: that emulsions are visible microscopically while colloids can only be resolved in the ultra microscope. Certain phenomena which can be observed in emulsions, for example, change in consistency upon storage or thickening, indicate plainly that some properties of colloidal systems are also present in emulsions.

An emulsion, therefore, consists in that either a solid body or a liquid is finely divided within another liquid. The finely divided substance is called the disperse phase and the external liquid is the closed phase or dispersion agent.

Here we are interested primarily in emulsions in which water is one phase. Here we distinguish essentially two types 21): Emulsions of the type oil-in-water, in which, therefore, water is the external phase, and emulsions of the type water-in-oil in which oil is the external phase.

These types of emulsions are basically different from each other since the external phase always decides the essential character of the emulsion 22), that is, an oil-in-water emulsion always bears the essential character of an aqueous liquid, while a water-in-oil emulsion is related to oils. In this case oil designates not only fatty oil but quite generally also mineral oil, thus, for example, lubricating oil, paraffin oil or turpentine oil, test naphtha and the like.

Now if two immiscible liquids are mixed together by violent shaking, for example, in a shaking machine, the liquids become very finely divided and a temporary emulsion is formed which separates again after the motion is stopped because of coagulation of the particles 23).

Flocculation is a result of surface tension or interfacial tension which causes both liquids to have a tendency to form the smallest possible surface so that the drops run together. If a third substance is added to the system before the shaking, which substance lowers the interfacial times between the liquids sufficiently, the emulsion state can be maintained through the formation of adsorption films in the surfaces for as long as is desired under suitable conditions. Such substances are called emulsifiers. In order to have the desired effect, they must be soluble in either one or both phases or at least must be wettable. In the oil and water system therefore the emulsifier must contain either hydrophilic groups or must be hydrophobic or lipophilic, that is, the oil attracting fraction must be so great that it is solvated by oil 24). It is therefore understandable that the emulsifier determines in general the type of emulsion. On the whole the statement is valid 25) that a water-soluble emulsifier favors emulsions of the type oil-in-water, and an oil-soluble emulsifier produces emulsions of the water-in-oil type. Thus, for example, with alkali soaps are obtained emulsions of the oil-in-water type, and with oil-soluble soaps having two or three valent cations, for example, aluminum, calcium and magnesium soaps, the water-in-oil type are produced. As a further example, it may be cited that the oil-soluble wool-fat alcohols favor emulsions of the type water-in-oil, while the fatty alcohol sulfonates, which have been made water soluble by the introduction of the SO₃H residue, again produce oil-in-water emulsions.

Aside from the type of emulsion it is of importance whether liquid or paste-like emulsions are obtained. Here the relationships are not yet so clear that they can be set down in generally valid statements. It is really surprising how little is found in the literature concerning this field which

yet is of very special interest to industry. For example, the following questions need clarification: (1) Why do tri-ethanolamine soaps in general produce liquid emulsions while with alkali soaps pasty emulsions are obtained? (2) Are there individual types of emulsifiers which produce liquid emulsions or is the entire emulsion, that is, the composition of both phases, of significance? (3) Is it possible, by a mechanical treatment which causes an increase in the degree of dispersion, to influence the viscosity of the emulsion so that with the same composition liquid or pasty emulsions result? In general, these are questions concerning viscosity of emulsions which undoubtedly are very closely related to similar problems of colloid chemistry.

These general statements on emulsions and emulsifying agents should precede the detailed discussion of the emulsifying agents which we developed from the wax acids. These present different special characteristics when compared with previously known emulsifiers. It may be especially emphasized that, as derivatives of the wax acids, they are completely fat free and are also free of such substances as can be used in the fatty acid synthesis; they are, therefore somewhat in contrast to previously customary emulsifying agents which are based almost exclusively on a fat material, for example, rapeseed oil, stearic acid, oleic acid, ricinoleic acid and the corresponding fatty alcohols and their conversion products, or on other natural substances such as lanolin, naphthenic acid from mineral oil refining, and the like. Accordingly, in a certain sense they represent something new and, therefore, render the properties to be discussed more closely explicable.

First the technical data will be explained. We, up till now, have developed three emulsifying agents which correspond to the three wax acids mentioned. They are designated as emulsifiers 1, 2, and 3. Emulsifiers 1 and 2 have been developed from wax acid 1 or 2 respectively and like the latter still contain 40-50% unsaponifiable in the form of unchanged paraffin. Emulsifier 2 has a hardening point of around 50° and emulsifier 1 has a hardening point of about 90°. Emulsifier 3 is prepared from wax acid 3, and like the latter is practically paraffin free, the hardening point is around 90-95°. Emulsifiers 1 and 3 are distinguished by a very extraordinary hardness.

The properties and possibilities of application of the emulsifiers are definitely influenced by the long carbon chain which they contain. This is the reason why they, although

basically hydrophilic, are still oil-soluble and thereby make possible the production of water-in-oil emulsions. The hydrophilic character is the reason that they are capable of absorbing water in appreciable amounts with the formation of stable emulsions of the oil-water-type, without themselves being water soluble. The emulsions are produced without further addition of alkali. They are always pasty in form, even in the presence of appreciable amounts of liquid in the form of oil and water. Concerning the production of liquid emulsions which resulting directly from the wax acids, there will be occasion to speak further hereinafter.

As a result of oil solubility together with a hydrophilic nature, therefore, as already mentioned with our emulsifier, we can produce both water-in-oil and oil-in-water emulsions. The principle that the emulsifying agent alone determines the type of emulsion can therefore no longer be maintained in its general application. It must be supplemented by a setting forth of the composition of the entire emulsion. This statement may be clarified by two examples for emulsions of different types: (1) A typical water-in-oil emulsion is obtained from the following mixture: 8% emulsifier 3, 17% of any suitable wax paraffin or ozokorite, 45% of oil, 30% water. (2) A typical oil-in-water emulsion for the following mixture: 8% emulsifier 3, 17% of any desired wax paraffin ozokorite, 8% oil, 67% water. Both are pasty and of similar consistency.

It is enlightening that it is also possible to prepare mixed emulsions in which, therefore, oil as well as water will occur as the disperse or closed phase. This can be proved among other ways through the fact that emulsions can be produced which can be colored with water-soluble and also with oil-soluble dyestuffs, thus simultaneously with water soluble methylene blue and a Sudan dye. To be sure, mixed emulsions have been previously described by different authors, among others Kadmer 26) and particularly by Clayton 27) who in his well known book on the theory of emulsions also mentions mixed emulsions but in that case two emulsifying agents always to be added one of which effects the oil-water emulsion and the other water-oil emulsion.

A further result of the constitution of the wax acid is that the emulsifiers even, in the acid range, have very good emulsifying actions. We were able, therefore, to regulate all of them so that the pH value of the emulsions lies below 7,

in general, between 6 and 7. For most purposes of application of pasty emulsions, this pH range is particularly desirable. In the section on the use of emulsifying agents more will be said concerning this.

In connection with this a little more can be stated concerning the production of liquid emulsions. As previously stated, the emulsifiers are only slightly suitable, for this purpose, preferably the wax acids are used and particularly those which are free from paraffin. In the manner similar to that with soap fatty acids, liquid emulsions with triethanolamine are obtained in the pH range of about 7. For certain purposes the emulsions must lie in the alkaline range; this is also possible to adjust with the wax acids, if the saponification is done with alkali particularly with potassium hydroxide or potassium carbonate. By the addition of an amount of alkali greater than that which is necessary for neutralization, emulsions are obtained which are semi-solid to fluid according to the amount of water and can be diluted with additional water without creaming. An example will be given later for this also.

To explain the phenomena which are connected with the production of solid and fluid emulsions, using emulsifiers and wax acids, very comprehensive experiments were necessary, which, moreover, have not as yet been concluded. The properties of the emulsions were only understandable in the light of the previously general explanations. For example, for fluid emulsions with completely saponified wax acids, as has already been stated for pasty emulsions with emulsifiers, it has proved true that the alkali salts of the wax acids are no longer soluble in water not even in colloidal form as, for example, are the alkali salts of the soap fatty acids; they are transformed into a sort of emulsoid-colloidal solution which is stabilized by excess alkali. The relationships are quite complex and are made more difficult through the difficulties of the experimental investigations; in part known methods of investigation had first to be revised until they were applicable to the high-molecular substances; in part reactions which of themselves are easily accomplished, had to be carried out under very special conditions, in order to attain the desired results. The high melting point of the wax acids and emulsifiers presented a particular difficulty concerning which more will be said later.

The hardening points of wax acids 1 and 3 are 80 and 90° respectively. In every case, therefore, before emulsification the material had to be heated in order to reach complete

solution in the other non-aqueous constituents of the emulsion. However, it has been shown that saponification also must be carried out in this temperature range in the production of liquid emulsions since the wax acids do not react sufficiently quickly with alkali at lower temperatures; for the same reason it is necessary that the saponification be carried out with very highly concentrated solutions, since only then is complete saturation to be reached. For emulsifiers 1 and 3 from the corresponding wax acids, the same holds true for solutions, and corresponding to the saponification temperature, the temperature for emulsification must also be selected very high.

Naturally, there will be cases where these high temperatures are not applicable; then, however, in most cases, wax acid 2 or emulsifier 2 can probably be used. However, where the high temperatures are not appreciably injurious, they signify no hindrance for the use of wax acids and wax emulsifiers because it is not a matter of the temperature of emulsion formation, but only how the emulsions behave at lower temperatures below the melting points of all components; that is, whether the solid substances are crystalline or amorphous, whether they have plastic properties or immediately become solid below the melting point.

For natural waxes there have been determined as particular characteristics: small crystalline structure, conchoidal fracture, great plasticity in contrast to the larger crystalline paraffins. It has now been proved by microscopic studies that the wax acids differ in crystalline structure appreciably from the paraffins and they also present marked conchoidal fracture. In particularly decided degree, however, the emulsifying agents and especially emulsifier 3 show these phenomena. They have, therefore, been designated quite differently from beeswax substitutes. It is therefore understandable if they act in emulsions with a smoothing and equalizing property. So far as we have studied our wax alcohols and wax esters, they show these qualities in increased degree. These entire questions, however, should first be postponed and should await a later study.

Now as it is desired to study more thoroughly the possibilities of use of the wax acids and emulsifiers, it is evident that only small selection of them can be used, which must be products capable of controlled addition. The wax acids, particularly because of their structure which is comparable to that of montanic acid, can be applied at practically all points to which refined montan wax and the acids prepared from crude

montan wax by refining can be used. The emulsifiers, as is evident from their properties, are suited to replace at many points the various emulsifiers built up from a fat basis.

In the first place will be discussed such products as now play a very important part and partially are even used in larger amounts and with improved properties. First will be discussed the production of lubricating greases and cutting oils. Lubricating greases (28) consist of mixtures of various soaps with lubricating oil and a little water; they can be considered as very concentrated emulsions which have a gel-like structure. In their manufacture formerly natural fats and fatty acids together with crude and refined montan wax were used exclusively and the saponification was carried out mainly with sodium hydroxide or lime. The amount of fat or fatty acid or wax was on the average about 10-30%. Since greases can be considered as water-in-oil emulsions and alkali greases as oil-in-water emulsions. It has now been shown that our wax acids, especially wax acid B, are suited in particularly good way to replace natural fats and refined montan wax in the manufacture of consistent greases. Since the wax acids cannot compete with natural fats in price, the manufacturer will be limited to the production of high priced greases and can here operate with relatively small additions, where greases are obtained which are very good in consistency behaviour even at low temperatures, show favorable aging behaviour, and have high flow and drop points in the order of magnitude of 140-150° and above. These greases moreover, because of slight water solubility of the saponified wax acid, due to the long carbon chain, possess an extraordinarily good water repellent capacity. Herein they exceed by far the consistent greases manufactured from natural fats. In this special field wax acids are not merely a substitute product, but they pave the way for entirely new developments in the production of greases which present properties heretofore unknown. In the case of cutting oils it is a matter of the manufacture of very highly dilutable emulsions in alkaline pH range in the form of oil-in-water emulsions. While formerly in the manufacture of cutting oils predominantly fat-containing emulsifiers were used for example soaps, Turkey red oil, sulfonated rape oil, whale oil or other natural products such as naphthenic acids, today it is necessary to use the fat free emulsifying agents so far as possible. Since naphthenic acids occur also only to limited extent and do not suffice by far for the necessary requirement for cutting oils, other fat free emulsifiers have been used, for example, the fatty acid foets which occur in the air oxidation of synthesis or raffin scale. With this, if fat emulsifiers are not used, are produced not cutting oils but cutting greases.

When wax acid 3 is used as an additive, in order to obtain a cutting grease dilutable in any practically usable proportion, 17 parts of wax acid are used with 83 parts of spindle oil, which is saponified with more than the theoretical amount of caustic alkali and to the saponified wax-acid mixture is added sufficient water that a cutting grease of satisfactory consistency results. For emulsification, a well operating stirring mechanism is necessary but not an emulsifying machine. Cutting grease can be easily diluted with normal tap water and produce stable non-creaming emulsions having a pH around 8-8.5 which according to Kadmer is quite sufficient for working iron and steel. Kadmer 29) in his book: "Machine Lubrication" states that the complete emulsion should have a pH value of 7.4-8.8 to avoid corrosion. Evidently it is possible for the purpose of increasing corrosion protection to add any corrosion inhibitor to the diluent water. If the water has a permanent hardness of more than 8-10°, it must be softened, since otherwise the lime soaps of the fatty acids precipitate and the emulsion is destroyed. Since for the production of cutting oils, fatty substance is also necessary to the amount of around 17-20%, an equivalent amount is released by the use of the wax acid.

Heretofore for the manufacture of cutting greases we have used the greatest variety of oils and have proved that in the selection of oils one is unrestricted. In general, it may probably be said that all oils, which are suited in practice because of their properties for the manufacture of cutting greases or cutting oils, will produce stable non-creaming emulsions with wax acid 3.

There is scarcely a doubt that the wax acids can also be applied to the manufacture of emulsion lubricating oils and probably also to emulsion lubricating greases. Some experiments show, for example, viscous mineral oil emulsions with 50% water can be prepared with the greatest variety of mineral oils, with viscosities from low up to very high. The emulsions obtained are very stable and even after standing for several weeks do not separate into oil and water. Tests are in preparation to study these viscous mineral oil emulsions for their use as additives to emulsion lubricating oils. By alteration of the alkali content, pasty emulsions can be obtained also with 50% water content which have flow and drop points at the order of magnitude of 50°C.

Further fields of application which at present are of great significance are the production of impregnating agents for waterproof fabrics and paper, also the production of carbon paper and the opening up of dye bases.

A further very important application is as a substitute for stearic acid, tallow and other fats in the leather industry. Here also mixtures of the different wax acids can be prepared corresponding to the intended use. Among the fields of application of emulsifying agents may be specially mentioned those in which it is a matter of the preparation of mixed emulsions, since they may bring particularly noticeable great advantages in this field, for example, in the manufacture of shoe dressings in emulsion form and in the production of pharmaceutical preparations. Of shoe dressings it is known that three principal types are distinguished: (1) pure oil dressings, (2) emulsion material in the form of mixed emulsions and (3) pure water dressings. Oil dressing consists essentially of about 25-30% wax component (including dye) and 70-75% turpentine oil-naphtha mixture. The emulsion product contains, in addition to these constituents, water amounting to from 30-40% with corresponding decrease of the turpentine oil-naphtha material, while the pure water dressing contains absolutely no organic solvent any more, but is composed only of wax and water. From well known facts emulsifiers are necessary for stabilizing the shoe dressings containing water. Formerly there were sufficient emulsifying agents available and the preparation of water-in-oil emulsions or oil-in-water emulsions offered no difficulty; since, however, the majority of such emulsifying agents were either direct derivatives of natural fats, as for example magnesium stearate, or had been prepared from natural fats or other natural products by a chemical conversion, a large number of them have disappeared because of present day necessity. With the emulsifiable waxes the difficulties of procurement increase continuously so that the manufacture of emulsifying shoe pastes today offers ever increasing difficulties. In this connection, however, it should be noted that the manufacture of emulsifying shoe dressing on a mineral oil base might result under certain circumstances in an appreciable saving of turpentine oil and heavy naphtha which in the manufacture of mixed emulsions could amount to several thousand tons of heavy naphtha in a year. Prerequisite for this naturally, is that a fat-free emulsifying agent shall be available which will answer all demands of industry. Here our emulsifying agents could probably be introduced with very definite prospect for success, since it is not only possible to produce the desired slightly acid shoe dressings with their help, but it also is possible to control in mixed emulsions the water-in-oil type which in its behaviour is extraordinarily similar to oil dressings and in many ways can be treated like oil dressings, for example, in the matter of packaging. The

production of emulsion shoe pastes is scarcely more difficult than that of an oil dressing, since it is possible to operate with a relatively efficient stirring mechanism and in any case does not require an emulsifying machine.

Also the preparation of emulsions which contain in addition to wax and water little or no turpentine oil or heavy naphtha, that is, therefore, pure water dressings, is entirely possible and likewise produces emulsions in the slightly acid pH range, but of the type oil-in-water. Whether such emulsions are to be considered as shoe dressings in the customary sense is another question, and is not under discussion here.

In the shoe dressings also the emulsifier fullfills a double purpose, since on the one hand it stabilizes the emulsions and on the other, because of its wax-like property it possesses qualities giving luster, so that further additions of polishing wax scarcely become necessary.

In the pharmaceutical field the emulsifiers described are good to use for the production of pasty emulsions because of their slightly acid character. Here there is also the further point, which may influence the suitability of an emulsifying agent, of the action of the emulsifier upon the skin. Investigations on this point have not as yet been finally concluded but according to present results it can already be stated that any skin injury is scarcely to be feared.

Summarizing, we can say that the wax acids developed by us and the wax emulsifying agents, wax alcohols and wax esters derived therefrom are of appreciable importance since in them for the first time is realized the idea of completely synthetic waxes 30) which are synthesized directly from coal. They represent, however, not only a substitute product, but are, in addition, probably no longer to be disregarded in peace time economy, since they with other synthetic products excell natural products in that they can be delivered with a completely uniform quality and the consumer does not need, as is still frequently the case in natural products, to take note of every batch because of the necessary changes in this formula, although they may be small, in order to arrive at the same end product. It is further of significance that products can be prepared with properties such as do not occur in natural products and, in addition, the properties can be relatively easily altered in a much larger range if the proposed utilization makes this necessary. The development of completely synthetic wax is not yet completed and for the future, further results may be expected which are of importance for the wax working industry.

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