GREASY COLD CREAMS.

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I doubt if there is a more popular toilet preparation than a fatty or greasy cold cream. Most every retail druggist has such a preparation under his own label. Many prefer to have these creams prepared for them by some manufacturing house, but there still remains a lot of druggists who will always prepare their own according to some "pet" formula they may possess.

The term "Cold Cream" probably originated from the fact that the evaporation of the moisture from them when applied to the skin gave a cooling effect.

The writer has recently conducted some exhaustive experiments with greasy cold creams and believes that some of his findings will be of great interest to the manufacturing pharmacist.

The pharmaceutical literature is filled with formulas for these creams, some of which differ considerably, and a great many of which give poor products. Let me state at the beginning of this paper that I am not going to give any formulas for making these creams, but will merely give you the results of my experiments and such suggestions as may help you in locating your source of trouble or in improving your formula.

At least four things are necessary to make a good cold cream, namely: 1st, white beeswax; 2nd, an oil; 3rd, a saponifying agent, and 4th, water.

Before taking up these different classes of ingredients, let us consider first

THE CHEMISTRY OF GREASY COLD CREAMS.

These creams are essentially emulsions. What, then, is the emulsifying agent?

We all know that soap has great emulsifying properties. If a soap is formed with the beeswax, and this soap acts as the emulsifying agent, then if the beeswax were omitted and castile soap, or any other soap, used instead, with enough ceresin to harden it, the resulting product should be a cold cream or emulsion. I have made such a cream, and while it is not a salable article, the fact that it was possible to make a cream in such a manner is good proof of the formation of a soap when beeswax is used.

If we mix the proper quantities of stearic acid, alkali, liquid petrolatum, water and an unsaponifiable hardening agent, such as paraffin or ceresin, an emulsion is readily formed. Here the alkali forms a soap with the stearic acid, and this acts as an emulsifying agent.

If beeswax is substituted for the stearic acid, we get the same results. Accordingly, we would conclude that there is present in the beeswax some constituent which will readily form a soap with as weak an alkali as borax.

According to Lewkowitsch[1] beeswax consists chiefly of a mixture of crude cerotic acid and myricin (melissyl myricyl palmitate). It also contains small quantities of free melissic acid and three or four other unimportant ingredients. The amount of this latter acid present is so small that we do not need to consider it.

[1] Lewkowitsch, 5th Edit. Vol. 2, P. 900.

According to Lewkowitsch,[2] free cerotic acid is present to the extent of 12 to 16 per cent, depending upon the source of the wax.

We know that solutions of borax, owing to the hydrolysis that takes place, react quite alkaline; that is to say, its solutions will contain a small amount of sodium hydroxide. When these aqueous alkaline solutions are brought in contact with the melted beeswax, all or a portion of the free cerotic acid is saponified. This soap then acts as an emulsifying agent for the balance of the wax and the other ingredients.

This equation may be represented thus:

$H.C_{26}H_{51}O_2$	+	NaOH	=	$Na\ C_{26}H_{51}O_2$	+	H_2O
Cerotic Acid		Sodium Hydrate (from borax solution)		Sodium Cerotate (soap)		Water

The other ingredient of beeswax, myricyl palmitate, ($C_{30}H_{61}.O.CO.C_{15}H_{31}$) probably is not saponified to any appreciable extent and more likely not at all by the alkaline borax solution, for such esters are very hard to saponify even with stronger alkalies and require considerable time to effect the change. In making cold creams the alkalinity of the borax solution is immediately neutralized by the cerotic acid, and it is therefore improbable that the myricyl palmitate enters at all into the chemistry of cold creams.

I desire to take exceptions to an article on "The Chemistry of Cold Creams," by Groat,[3] who claims that borax reacts with the myricyl palmitate and with the glycerides of other oils and fats to saponify them. The preceding paragraph will show my reasons for differing with him in this respect.

To continue, in the same article Groat gives an equation showing the reaction of the borax and water upon the myricyl palmitate in which he claims palmitic borate is formed. As he does not mention anything at all about the soap that is formed (sodium cerotate) one would conclude that this was his idea of the reactions entering into the manufacture of cold creams. He could not have tried to prove his statements by experiments, for he goes on to say, "We shall now take up the reaction of borax with spermaceti. The chief constituent of spermaceti is cetincetyl palmitate, which is attacked by the borax forming palmitic borate, as in the case of white wax, etc." Here again his idea is the formation of an ester (palmitic borate) by the borax. Let me say right here, that you cannot make a cold cream from spermaceti unless you introduce soap by some other means, for spermaceti does not contain more than traces of free acid and therefore could not form a soap of itself. Palmitic borate does not exist to any extent, if at all in cold cream, and Groat's statements are in my opinion, erroneous. To sum it up, I would say that he has overlooked the presence of free acids in the wax which form soaps with the alkaline borax solutions and instead has given the impression that organic esters were formed. Supposing one should use sodium carbonate or sodium citrate instead of borax. These both form cold creams with wax. Then according to his theories the resulting cream would consist of palmitic carbonate or palmitic citrate. Perhaps he did not know that a cream could be made from these above named substances. I have prepared such creams.

[2] Lewkowitsch, 5th Edit. Vol. 2, P. 905.

[3] Journal of the A. Ph. Assoc., Feb., 1915, P. 169.

Both the carbonate and the citrate give aqueous solutions which are alkaline. According to the Hydrolytic Dissociation Theory we would not expect sodium citrate to give as strongly alkaline solution as the carbonate and could not therefore expect as much soap to be formed or as good a cream as when the borate or carbonate are used. We find such to be the case, but there is enough soap formed to prove that the emulsification of the cold cream is brought about by the soap rather than by the formation of any esters.

Only such fats and waxes as contain free acids can be used to form soaps with the borax solution. Those fats and waxes which are free from acid are only valuable as stiffening agents. You will then see that beeswax or some other such product which has *an acid value* is absolutely necessary in order to make a cold cream.

The acid value indicates the number of milligrams of potassium hydrate required to saturate the free fatty acids in one gram of a fat or wax, and is therefore a measure of the free fatty acids in a fat or wax.

It is evident that if an oil or fat consists exclusively of neutral triglycerides, its acid value will be nil. We would not expect such a fat or wax to yield a soap or to act as an emulsifier for the balance of ingredients.

Lewkowitsch gives the following acid value for the several fats or waxes:

	Acid Value
Carnauba Wax	2
Japan Wax	20
Spermaceti	traces
Beeswax	20
Tallow	4
Paraffin	0
Ceresin	0

According to my theories then, one could not make a soap from paraffin or ceresin and a solution of borax or any other alkaline solution. Consequently a cold cream could not be made from these substances unless wax or some other substance containing free fatty acid is added. From the above table we would not expect spermaceti to act any better for it is, according to the above, a practically neutral substance. Tallow and Carnauba wax will however make an emulsion, but as the quantity of soap formed is very small the cream is not smooth, or in other words, the emulsion is not very good. Japan wax and beeswax we would expect to yield good creams. Experiments made in the laboratory prove this to be so, although I do not recommend Japan wax to you for use in your creams, because it has a lower melting point and more color and odor than beeswax. These statements are offered as further proof that a soap is formed in making cold cream and to show that only those substances containing free acid will make an emulsion when the borax solution is added.

Let us now pass on to the first class of ingredients necessary to make cold cream, namely:

HARDENING OR STIFFENING AGENTS.

Beeswax as you all probably know is secreted by the common bee, *Apis mellifica.* Honey is removed from the combs by centrifugal force. The wax is then obtained by melting and straining or by expression. The expressed wax is as a rule of a yellowish color and has to be purified, followed, if required, by a

process of bleaching, either by air and light or by chemical agents which will yield nascent oxygen.

The best bleached white wax is of a pure white or only slightly yellowish color. The whiter the wax you use in your cream, the whiter the cream will be.

It can be definitely stated that white beeswax is absolutely necessary to every first class white cold cream. It supplies the soap necessary to form the emulsion and gives the smoothest cream of any of the waxes. It should be present in sufficient quantity to give the cream the desired stiffness. However, white wax is quite an expensive substance and a part of it can be replaced by other substances such as spermaceti, paraffin or white ceresin. In making such substitutes one must bear in mind that a certain amount of white wax is necessary to make the emulsion and when too much of the white wax is replaced the creams are not smooth and in some cases there is a tendency towards separation of the emulsion. I would advise you not to try to take out too much of the white wax.

Spermaceti, then, is only valuable as a stiffening agent, because it does not form any soap. It is also quite expensive and has a low melting point (45°-50° C.) More of it is therefore required to accomplish the purpose than is required of either paraffin or ceresin, consequently it is an expensive and unnecessary ingredient. Six samples of cream were made containing varying amounts of spermaceti. The ones containing the least of it were easily selected as being the smoothest, but none of them were as smooth as when the spermaceti was omitted entirely. I would therefore advise that spermaceti be omitted from your formula and that paraffin or white ceresin be used instead.

Paraffin is useful as a stiffening agent. Too much of it cannot be used as it will interfere with the smoothness of the cream.

White ceresin is an excellent stiffening agent when used in conjunction with white wax. Ceresin (osokerite) is a natural earth-wax or hydrocarbon. When purified and bleached it is a snow-white solid resembling paraffin in its properties. It has considerably higher melting point (about 62° C.) than paraffin, consequently less of it is required to produce the same amount of stiffening. It is a little more expensive than paraffin but much less so than spermaceti. Like paraffin, it cannot be used in too great a quantity.

Stearic acid is sometimes used as a stiffening agent, in small amounts. It permits of the incorporation of more water and thus gives a whiter and less greasy cream. It has the disadvantage of making the cream granular in time, even if very small amounts are used. If the smoothness of your cream is a desirable asset, don't use stearic acid.

When creams are to be sold in warm climates more stiffering agent is required.

THE OILS.

Two classes of oils are sometimes used: the vegetable and mineral.

The vegetable oils are said to be absorbed better by the skin than the petroleum oils, and therefore are preferred in medicinal creams. Expressed oil of almonds, peach kernel, castor, olive, cocoanut, cottonseed and sesame oils are frequently used. The objection to them is that when emulsified, they quickly become rancid. Also they impart an odor which is objectionable and do not yield the whitest of creams.

Lanoline is sometimes used, but its odor and color are objectionable. If a white cream is desired, it cannot be used at all. It has the advantage of being easily absorbed by the skin.

This brings us to the mineral or petroleum oils. These oils can be secured in a variety of grades differing in color, odor and specific gravity, according to the price you wish to pay. It is not necessary to buy the Russian mineral oils for creams. American oils are cheaper and good enough grades are obtainable. To make the best cream, the oil should be colorless and with as little odor as possible. The specific gravity may range from .860 to .880. One gives as good a cream as the other, but the one of the higher specific gravity requires less stiffening agent.

A snow-white mineral jelly or petrolatum may be used in creams for warm climates. If used in other climates less stiffening agent should be used. One does not need to pay the price asked for these jellies for they are not natural jellies but are made by solidifying the mineral oil with white ceresin. All you would have to do to obtain this same effect would be to increase the amount of white ceresin in your formula.

The claim has been made that mineral oils induce the growth of hair. The writer believes that this is without foundation and the public have a wrong idea of the matter, which is traceable to unscrupulous advertisements. If there is any growth of hair, it more likely comes from stimulation of the hair cells through massage.

Cold creams made with mineral oil are permanent and do not turn rancid.

THE SAPONIFYING AGENT.

Borax is the best for this purpose. This salt is a combination of a strong base and a weak acid. When dissolved in water, it undergoes hydrolysis, yielding solutions which are distinctly alkaline to litmus. This alkalinity is neutralized by the cerotic acid of the wax forming the soap which in turn acts as an emulsifying agent for the balance of the ingredients.

Creams can be made with any other substances whose solutions react alkaline. Those made with potassium salts are softer than those made with sodium salts.

Borax gives the best and smoothest cream and is to be preferred over all others.

The fourth essential ingredient is

WATER.

Distilled water is always to be preferred, although tap water can be used if it does not contain much calcium or iron. The proper amount to use is an important matter. No matter what the ingredients you select or how good the quality, unless you use them in the proper proportions, that is, have your formula properly balanced, your cream will not be the best possible to obtain.

I have analyzed several cold creams on the market and found them to contain from 22 to 40% of water. The one containing 40% was the whitest but the least smooth of any and contained some stearate; otherwise this high percentage would not have been possible.

It might be said here, that the water is what makes the cold cream white. The more water, the whiter the cream of course, but too much water makes the cream granular and may cause a separation.

My experiments have shown 25% of water to be the proper amount to use from a manufacturer's view point. I have observed such samples during two years and find them to keep perfectly without separation or granulation.

THE PERFUME.

The perfume is added just before the cream is drawn off into the containers, otherwise a portion of it is volatilized by the heat. The perfume should not contain much alcohol as the alcohol has a tendency to break up the emulsion, especially when hot.

Rose, Lilac and Violet are the most popular odors, the rose predominating. Rose and Violet are quite expensive. Lilac is one of the cheapest.

Let me caution you about lilac perfumes for creams. Most of them excepting perhaps a few expensive ones, contain quite a bit of terpineol. Some of you may be using terpineol itself as a perfume. This substance is very irritating to the skin and should not be used in cold creams. Synthetic perfumes are more often irritating than natural oils. If you have complaints that your cream irritates the skin, the first place to look for the trouble is in your perfume.

One other thing about perfumes. They often cause discoloration of the cream, sometimes even making the cream decidedly brown.

The discoloration by the perfume must be distinguished from the loss of whiteness that comes from the cream drying out. To test this, make up two samples of cream from the same formula. Perfume only one of them. Preserve them under the same conditions in the same kind of containers. After standing awhile they can be compared. If the perfume sample is noticeably more discolored than the other, the trouble can be attributed to the perfume.

THE CONTAINER.

Collapsible tubes are by far the ideal, as the cream does not dry out and they are more sanitary.

Collapsible tubes are not as attractive to the trade as jars and are not as convenient for the druggists to fill.

Jars with screw tops are therefore the most popular. You cannot be too careful in selecting your jars. I refer particularly to choosing a jar which has a tight-fitting cover. The covers should require at least a full turn to tighten them and extra precautions such as a paraffined card-board washer should be used. In fact, you should aim at having your jar as nearly hermetically sealed as possible. The reason for this is very simple, yet it is the cause of many a druggist's or manufacturer's difficulties. Cold cream contains water, which cannot help but dry out if improperly protected. As the cream loses water, it loses its whiteness and takes on a lardy appearance. It shrinks in the jar and pulls away from the sides. The result is soon only a partly filled jar.

The cream should be poured into the jars while still liquid and at as low a temperature as possible to prevent too large a hollow being formed in the center. A better surface can be obtained by warming the jars before filling them with cream. This permits of a more even cooling of the cream, whereas when poured into a cold jar the cream cools around the sides and bottom first. As it cools it contracts and forms the hollow in the center and may cause a pulling away of the cream from the sides of the jar.

PINK CREAMS.

Colored creams are novelties. A pink cream with a carnation perfume is quite popular just now.

These are made by dissolving a small amount of an oil-soluble color in the melted fats before adding the borax solution. The latter is not to be colored.

To make a pink cream, use the dye known as Oil Red S.

THEATRICAL COLD CREAMS.

These are cheaper creams and are usually sold in large packages. They may be softer than an ordinary cream. A cheap grade of mineral oil can be used. They are not intended for toilet purposes but for "make-up" use and therefore do not need to be of as good a quality.

TROUBLES YOU MAY ENCOUNTER.

Cream is not smooth. This may be due to a poor formula or to improper care in mixing.

Lack of whiteness. The wax may not have been very white or the cream may have lost some of its water.

Separation of water indicates either carelessness in mixing or more likely a faulty formula. Perhaps your formula contains too high a percentage of water.

Cream appears lardy after standing some time. Indicates loss of water. Covers do not fit tight enough.

Shrinking in the jars indicates loss of water.

Pulling away from sides of jars. If this takes place within a few days it may be due to improperly balanced formula or to pouring the cream too hot or to using too cold jars. If it does not take place for several weeks, it is probably due to loss of water.

Discoloration. This is almost always due to the perfume. The use of iron utensils may also cause discoloration.

Cream separates. May be due to the jars standing in the sun or in too warm a place.

CONCLUSIONS.

1. Greasy cold creams are essentially emulsions, brought about by the formation of a soap by the alkaline borax solution and the free cerotic acid of the wax, the soap acting as an emulsifying agent.

2. White beeswax, paraffin or ceresin, colorless liquid petrolatum (mineral oil), borax and water in proper proportions form the best creams.

3. Creams made from the above ingredients are more permanent than when vegetable oils are used and do not turn rancid.

4. Much attention should be paid to obtaining tight-fitting covers for the jars to guard against loss of water.

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