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ADVANCES IN SOLVENT
DEWAXING OF MINERAL OILS AND TARS

By Dr. Karl A. Fischer

A R T I C L E III

CRYSTALLOGRAPHIC CONCLUSIONS

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The waxes of various type from the described fractionations were examined under the microscope. With regard to solvent dewaxing we only studied the behaviour of paraffins separating from chilled solutions in chlorinated hydrocarbons or other organic solvents. It is emphasized that waxes may behave differently when crystallizing at elevated temperature or from their melt.

From any diluted solution and at low temperature the paraffins always crystallized in plates, probably of the rhombic system, regardless of molecular weight and chemical structure. Hexagon shaped plates were frequently observed, but they must also be classified as rhombic, because they were doubly refracting in direction vertical to the hexagonal plane. That excludes short prisms of the hexagonal system, looked upon in direction of the c-axis, which as an optical axis is isotropic. The tiny plates of high molecular waxes of any type were also optically biaxial, but no other confirmation of the crystal system could be obtained.

For the problem of solvent dewaxing it seems to be uninteresting to discern between needle waxes and plates. Even if paraffin plates may appear to have needle shape under certain circumstances, as we shall see, they have never well proportioned prismatic form and should with regard to the important capillary considerations be conceived as plates.

The most evident difference of various paraffins is in crystal size. There seems to be a general rule, that the size of wax crystals is largest for the highly branched, low melting waxes of low molecular weight. The crystals grow

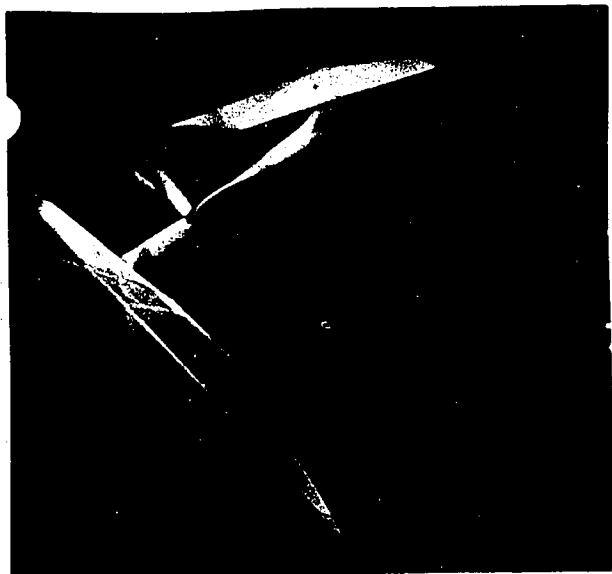
less readily with increasing molecular weight and with rising melting point. Its growth is obviously inhibited in all three dimensions for high melting cyclic compounds and high molecular n - paraffins, finally leading close to colloidal dimensions.

Although that may sound absurd it is therefore practical to classify the waxes according to average size of their crystals, which in contrast to most other known substances is not very much influenced in its order of magnitude and for maximum growth by external influences, which would cause other chemicals to grow crystals of any size.

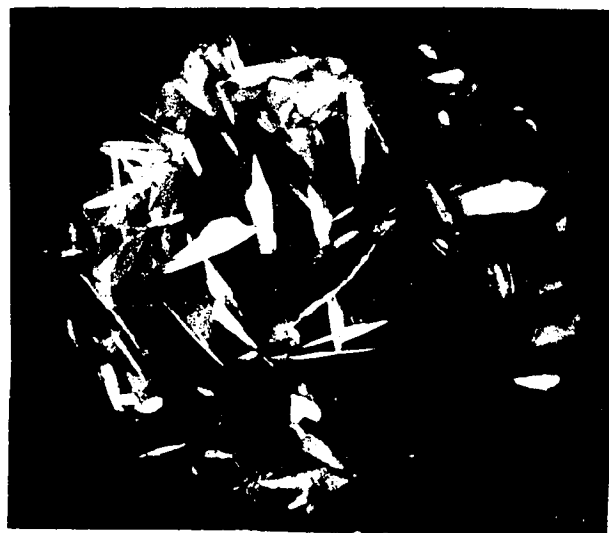
Five types of average crystal size were coordinated to the spaces in the graph (article II). Such plates crystallize under ordinary solvent dewaxing conditions, and size and shape of the crystals is only little influenced by wide variation of dilution, extension of chilling time above a minimum limit and kind of solvent.

Although no fundamental change in crystal system seems to exist for various paraffin waxes, the crystals may come out in various shapes from cooled solutions. Large size plates are typical for low molecular paraffins, but the crystals take the shape of a dissecting knife or needle for average molecular waxes and appear mostly to be needles, for high molecular ones. Still they are plates and the needle form results from inhibited growth, from fractional dissolution or it is pretended by the peculiar optical behaviour of the extremely thin and flat crystals. No well defined prisms could ever be observed on any wax, although crystal habit and size was studied in dependence from chilling time, solvent, evaporation of solvent instead of chilling, contaminants and dilution.

Microphotographs 30 x of the five discussed wax types
of different molecular weight and structure, classified
as A, B, C, D, E in the graph. All are plates. The needle form
of C, D and E is illusion.



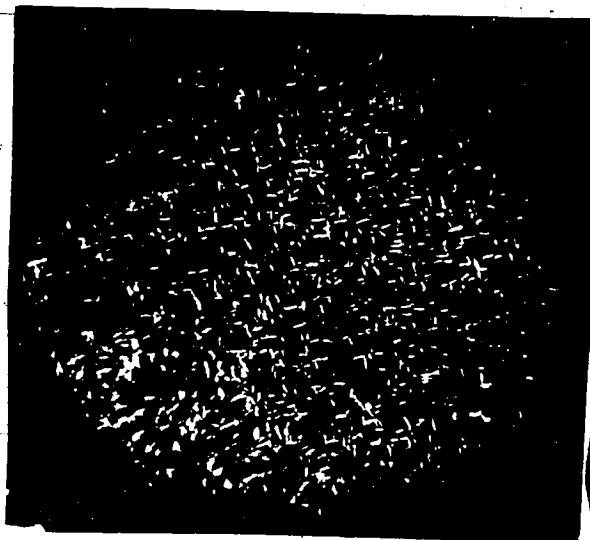
A > 1000 μ



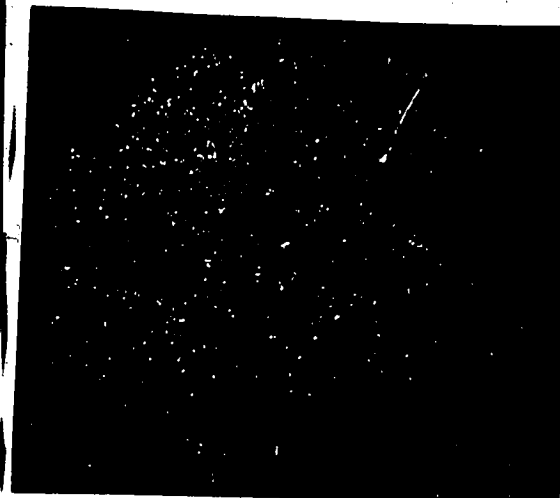
B ~ 300 μ



C
~ 100 μ



D
~ 30 μ



E
< 10 μ

Paraffin crystals are always very thin, even so for the large plates of soft waxes and naturally thickness therefore, can only vary within narrow limits. Double refractivity is low, as it can be concluded from the wide spaces of Cassini's curves in conoscopic examination. It increases only little for waxes with higher molecular weight and more isomeric or cyclic structure. (Article VII).

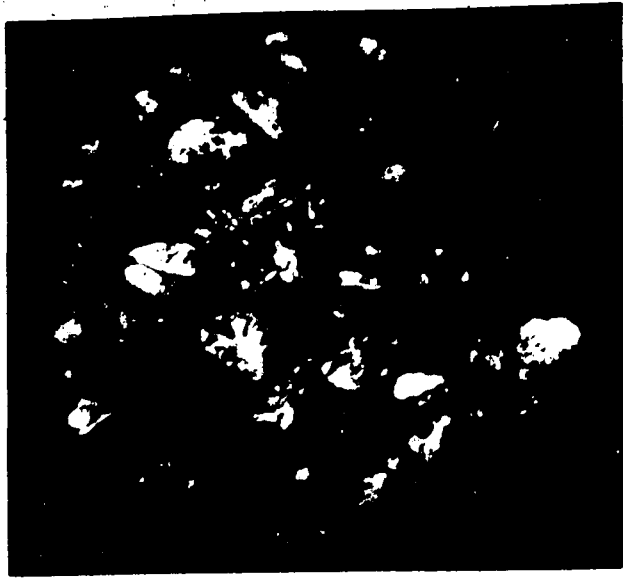
There exist two optically isotropic axes, one of which runs almost vertical to the largest crystal faces. Considering also the angle of extinction it is obvious, that a large number of thin wax crystals in a preparation will remain invisible between crossed nicols. Thicker plates are sufficiently optically active to show even if they are preferably arranged parallel to the supporting slide, but smaller and thinner plates when arranged above each other frequently counteract in polarization and will not show even with the help of a gypsum plate, red I order. Plates which are arranged in a steep angle to the supporting plane, or which are observed edgewise, have maximum double refractivity and therefore show very brightly. They frequently pretend needle shaped crystals even when well grown plates are present. This illusion is predominant for high molecular paraffins in which thickness and therefore optical activity is trivial. By tricks in illumination it is easy however to make all crystals plainly visible and the appearance is usually considerably changed if the below described combination of polarized light with dark field illumination and stereoscopic attachment is used. Observation between slide and cover glass is to be preferred to the hanging drop method in which more and larger plates arrange radially to the microscope axis, underlining the needle impression. Gently pressing and releasing of the cover glass improves visibility sometimes.

Those facts must be specially considered if a comparative study is made about the improvement of a waxy fraction by physical or chemical treatment in which the average molecular weight is not changed substantially. The usefulness of microscopic examination may be demonstrated on a raw brown coal tar which in its original state would have offered very much difficulty to any dewaxing method. It contained preferably low molecular branched paraffins as it was evident from the graph described above and also all sorts of impurities, which influences the growth of the undoubtedly plate shaped crystals. No defined crystal angles could be measured. (Picture I, page 38). The tar was submitted to atmospheric distillation, which removed the impurities, especially the readily absorbed colloidal ones. Instable iso-compounds split off side chains and the micro-picture reveals that large plates with poor defined boundaries, attributed to branched paraffins, are present besides a few well defined crystals of normal waxes. (Picture II, page 38).

The same distillate was then submitted to two more atmospheric distillations with less caution and under slight cracking, and the picture is entirely different. The isoparaffinic molecules were completely broken down which was indicated by slightly lower average molecular weight and very low classification numbers. The microscope shows a multitude of crystal plates which are smaller in average but have well defined boundaries. (Picture III, page 38). It is evident that such a wax will offer less difficulty in removal than the primary product. Things are not always as plain as in this example.

For high molecular and cyclic waxes the microscopic examination will seldom indicate a substantial change after any sort of treatment. Of course, that may be attributed to little chemical changes in structure. Rough treatment by cracking will always reflect in crystal behaviour.

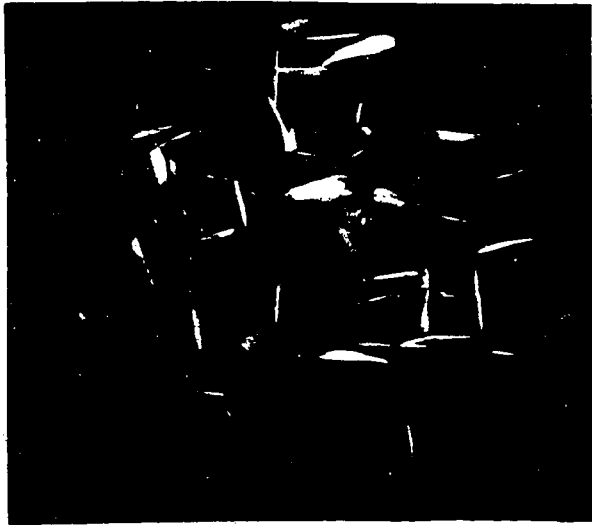
PICTURE I



PICTURE II



PICTURE III



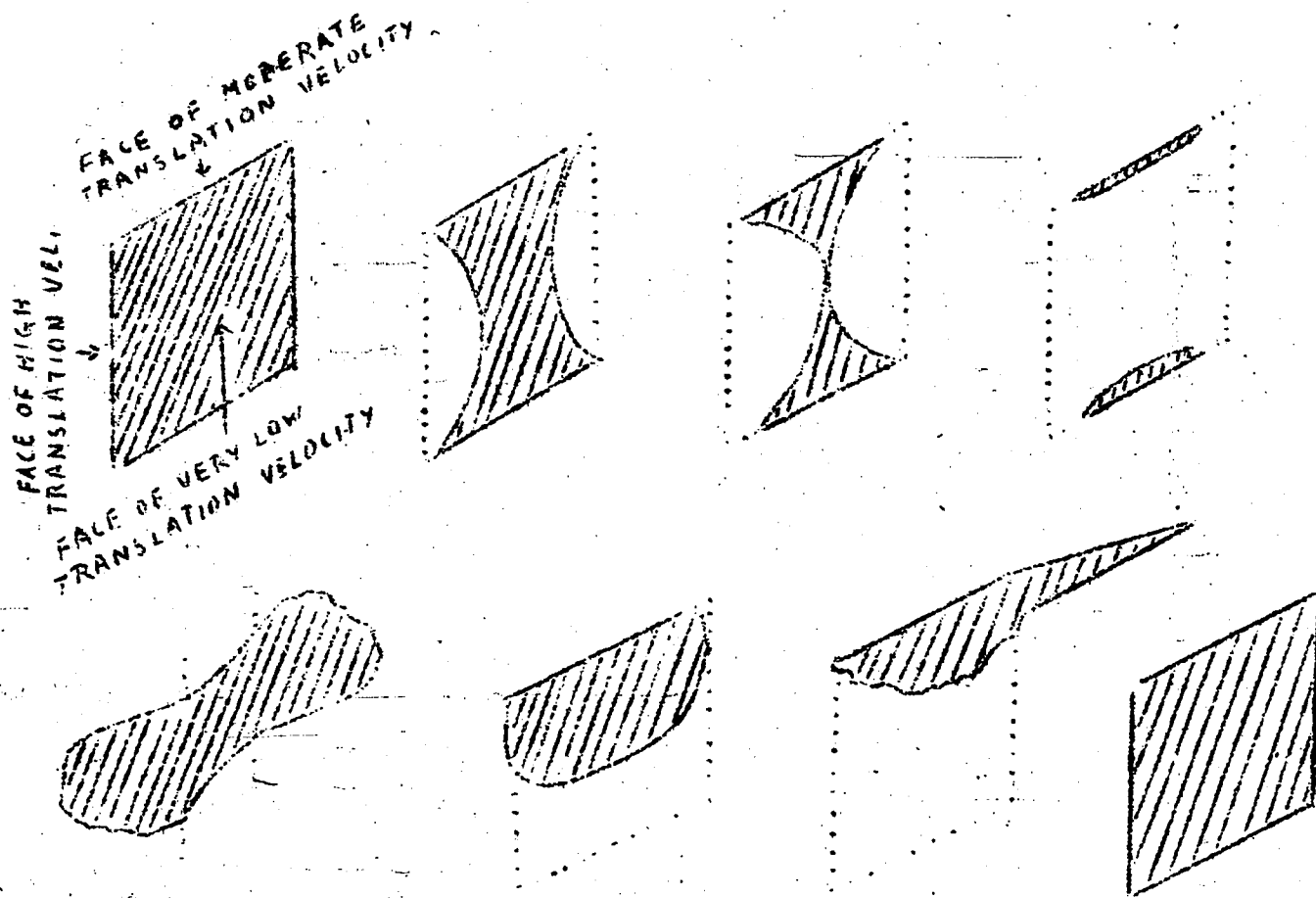
Thick plates have obviously smallest surface for a given quantity of wax, which is of importance with regard to surface adsorption and deoiling. Thin plates, needles or fine granular precipitates will naturally have much inferior properties with regard to the production of entirely oil free wax. The growth of paraffin crystals was therefore closer studied with the aim to cause wax crystals to grow thicker. Solvent, dilution, chilling rate and addition of chemicals are known to influence crystal growth, but while it was possible to influence size and shape of lower molecular waxes slightly, there was experienced the greatest difficulty in any effort to make high molecular waxes grow larger crystals. It is in contrast to most of the well known crystallized substances of inorganic or organic chemistry, which grow readily and more or less evenly in all three dimensions, that paraffin crystals neglect growth in 1, 2, or all three crystalline axes. For example it is easy to grow crystals of soft low molecular normal or isoparaffins in plates which cover an area of almost a square inch, but those crystals will always be extremely thin and hardly exceed the thickness of a few hundredth of a millimeter. Thickness will also refuse to increase if crystallization is extended over a period of months and from very diluted solutions.

It was interesting to observe how paraffin crystals behave in dissolving and recrystallization. Increase of temperature of a fraction of a C° shows that 2 crystal faces have exceedingly high translation velocity. Thickness is little affected and the plate shrinks to 2 needle shaped crystals. If temperature is then cautiously lowered, it is the same two faces which grow in rapid rate where they decreased before. The thickness, as neglected dimension again grows extremely slow as it can be concluded from the shade of the color of polarization. There were indications that the same fact holds true for higher molecular waxes, but large experimental difficulties were involved in observing those tiny, tender crystals, which disappear just too readily as soon as crystal decomposition starts.



The variety in the shape of wax crystals, from plates to needles, and the appearance of mal grown crystals is therefore caused by the fact that one crystalline axis grows or dissolves only negligibly, while the second one may grow normally and the third one with extreme rapidity. Growth in either direction may be inhibited by absorbed matter.

Appearance of dissolving and of growing paraffin crystals



See microphotographs page 40.

This explains why it is practically impossible to obtain a substantial improvement of the charging stock by tricks in chilling, and accounts for the appearance of needle shaped plates for reason of temperature fluctuation or inhibited growth. Those mutilated plates have definitely bad filtering quality which indicates that any substantial warming of the charging stock between chillers and filters is to be avoided. That needle shape is not to be confounded with true prismatic needles which may grow from melts at a transition temperature.

Crystal faces which grow and dissolve very rapidly may also be surfaces of preferred adsorption for impurities, alien matter and oil. If they are coated with any such chemical they cannot grow further, leaving just one crystalline axis or part of a crystal face open for growth. High viscous oil of high molecular weight is naturally preferably adsorbed which accounts for a certain influence of viscosity. Needle shaped tender crystals may then result, especially since the growth of smallest crystal faces is preferred anyway. We take that as a plausible explanation for the effect of pour point depressors, which, by adsorption, cause filiform monodimensional crystal growth, blocking growth of crystal faces. Such a structure is then unable to support the oil which will therefore pour at much lower temperature.

Experience in commercial plants has shown that a certain chilling rate is required for good filtration which is roughly $0.5 - 1 \text{ C}^{\circ}$ per minute. Further extension of chilling time beyond that rate did not give a noticeable improvement of the charging stock. There is naturally a limit which prohibits making chilling time too short. By rapid chilling the crystals will have no chance to grow as big as they can, and the procedure is known to give crystals of particularly small size which is sometimes desired in chemical manufacturing to avoid inclusions and to obtain products of higher purity. For the dewaxing

of oils and tars it is worthless, however. The size of wax crystals can also be cut down to colloidal dimensions by shock chilling. This subject was studied with regard to dewaxing by diffusion. It proved to be of no interest for any dewaxing procedure. The desire for well built and large three dimensional crystals will continue to exist in dewaxing practice because such crystals will favourably influence filtration speed and efficiency of cake washing. Research may find a way to accomplish that, but it will then be a basically new procedure. Addition of all sorts of dopes inhibited crystal growth instead of promoting it and the possible ways which may lead to the target are limited.

The different behaviour of various waxes with regard to crystal shape and size make it particularly difficult to fix standard dewaxing conditions for long cuts and long residues in which the paraffinic components spread over a wide range of molecular weight. Narrow cuts or filtration in steps is more accessible to study. The problem is further complicated because it is not the crystallographic view point only, but also phase rule considerations which govern dewaxing, as it will be described later.

We mentioned above, that no fundamental influence can be exerted to cause the high molecular waxes to grow larger crystals or to influence thickness of lower paraffin plates. But crystal size can be cut down in its order of magnitude by rapid chilling or adsorption. High molecular and polar compounds will evidently be most effective, which accounts for preferred adsorption of distillation bottoms, high viscous oil constituents and synthetic dewaxing dopes. That gives us one possibility to influence the structure of a filter cake. The influence will obviously be most evident for the average molecular paraffins, because wax from lower fractions is obtained well crystallized without difficulty and the high molecular waxes grow too tiny crystals to notice a remarkable effect.

It is just the average molecular and long cut which occasionally, and depending upon origin and solvent, gives voluminous swollen filter cakes. This is probably caused by numerous thin bent and curled or folded plates which have naturally a maximum of capillary spaces and therefore retain oil or solvent stubbornly, giving very poor filter rates. That is one example where inhibited plate growth by adsorption gives a remarkable improvement. The crystals then grow smaller indeed, but they are better 3 dimensionally shaped and therefore do not curl or bend, taking less space and making the filter cake more compact. The effect may be compared with a piece of paper foil, which when crumpled and wadded up represents the spacious swollen structure, whereas it occupies considerably less space when it is torn to pieces which are more or less regularly stapled.

Vice versa it is evidently also possible that a charging stock which carries well shaped crystals when clean, may be considerably deteriorated by carry over of heavy oil in distillation.

The problems, which are involved in filtration and washing of the filter cake concern filtration velocity and filter cake thickness. In the following we presume that dewaxing is done in homogeneous phase and that the filter cake is evenly built up and penetrable.

The wax solvent slurry can neither be called granular, nor slimy. It has both properties combined and is coarser in texture for light cuts and more colloidal for heavy cuts.

CAKE THICKNESS:

Consumption of wash liquid is determined by 2 factors, a) oil retention in the capillaries and b) the removal of adsorbed oil from the wax crystals.

a) The liquid in the capillaries is just pushed ahead and replaced by solvent. Solvent consumption is therefore proportional to cake thickness, if

the cake is to conserve its liquid/solid composition. The influence of crystal size is minute.

b) The removal of adsorbed oil is a leaching process. Because the thickness of the filter cake is always comparatively small it is advantageous to consider it as a multiple batch extraction with clean solvent, which is especially a close approximation to operating conditions in the below discussed band filters. The effect of n batch washings is then expressed by the formula:

$$O_n = O_o \left(\frac{k \cdot C}{k \cdot C + S} \right)^n \quad \text{or} \quad n \cdot \log \left(\frac{k \cdot C}{k \cdot C + S} \right) = \log \frac{O_n}{O_o}$$

in which O_n means retained oil after washing, O_o originally adsorbed oil, k coefficient of distribution, C adsorbing crystal surface, S quantity of solvent. This process controls chiefly the consumption of wash liquid and it is evident that crystal size, given by C is of considerable importance. So is k , which reflects the forces of adsorption but seems to be of the same order of magnitude for light and heavy fractions. C naturally also increases proportionally to the thickness of the filter cake, and consumption of wash liquid is therefore also in case b) proportional to filter cake thickness. Thicker cakes would not be objectionable and may even be advantageous with regard to the countercurrent washing effect, but there are limits given by decreasing permeability due to compression and other growing unfavourable influences, which become noticeable between 2 - 6 cm for light cuts and 1/2 - 3 cm for heavy cuts.

High molecular waxes will retain more solution, caused by the fine granular structure which accounts for larger adsorbing surface and more capillary spaces. Washing of those cakes therefore requires more solvent. Solvents with low surface tension should theoretically have advantages because they are more readily tied to the crystals by forces of adhesion, than oil or other solvents. That would

mean, that heterocyclic compounds and aromatics are slightly inferior as solvent to ketones or chlorinated hydrocarbons. The esters, monovalent alcohols and ethers cannot be considered, although their surface tension is still lower, because they have pronounced selective properties. In any case the difference in surface tension is only small and probably without visible influence.

FILTRATION RATE:

The structure of a filtercake determines its porosity and the rate of through-flow of liquids. It is evident that fine granular wax cakes have more and smaller pores than scaly ones and offer higher resistance to penetration of liquids, similar to fritted glass plates of coarse or fine mesh glass powder.

It is not possible to express mathematically the flow rate of liquids through layers of tiny crystals with varying and little known dimensions of capillary spaces. Very much simplified our system may be considered as consisting of a multitude of parallel planes in which capillary distance is determined by the spacing crystal thickness " x ", the width by crystal diameter " w ", the length " L " as a function of filter cake thickness, " N " the number of capillaries, per square area unit depending upon crystal size, " p " is suction pressure C a constant and " η " means viscosity. Then filtration rate may be expressed by a known formula for viscous flow between parallel planes as;

$$F.R. = \frac{x^3 \cdot w \cdot p}{C \cdot L \cdot \eta} \cdot N$$

Capillary bends, turbulent flow and many other important factors are neglected. The formula reflects the dominant influence of crystal thickness, which spaces the capillaries and enters the formula in the third power, in contrast to all other figures which influence the result linearly only. This however confirms the assumption, that crystal thickness does not change very much for any commercial wax which has been precipitated from solutions. A substantial change in

crystal thickness would show in filtration rates hundreds of times higher
or lower, inversely to the third power of crystal thickness. Experimentally
it has been found however, that filtration rate in extreme cases, that is,
between light cuts with large crystals and heavy distillates or propane deas-
phaltized residues, does not differ more than 1 : 20 for equal dilution, wax
content and cake thickness.

Under unfavourable conditions it is obviously possible to cut filtration
rate of any wax down to practically zero, but that has nothing to do with proper
dewaxing, although it shows the influence of x^3 if the crystals are grown pur-
posely much smaller than they would under proper dewaxing conditions. The other
figures of the formula are only of little determining influence. All those term
depend on crystal size, η indirectly only, because smaller crystals go with more
viscous oils; w decreases linearly with increasing number N of crystals and the
numerator is but little changed. The denominator does not change substantially
either. L decreases somewhat because smaller crystals mean more bends but a
shorter way for the liquid flow after all. This is compensated by an increase
of viscosity η . Naturally this consideration is supposed to show changes in the
order of magnitude only.

The thickness of the filter cake is of linear influence, for any given
charging stock and inversely proportional to filtration time.

X^3 , and c have little influence and p is supposed to be constant. The
numerator in the equation remains constant because the width of the crystals
is not changed and the number of capillary spaces per square inch is also the
same. L is influenced proportional to cake thickness while viscosity also
remains constant. It is the denominator only which therefore controls the
equation linearly for varying cake thickness. This seems plausible when compared
with experimental results. For light and medium cuts it was found that filtra-
tion time was in average cut to half, if the thickness of the filter cake was

doubled. (For cake thickness 1 - 4 cm). For heavier distillates the results varied because slight experimental irregularities influence the delicate systems considerably. In average a nearly linear dependence of filtration rate from thickness of filter cake can be assumed however, within the limits, which were given above.

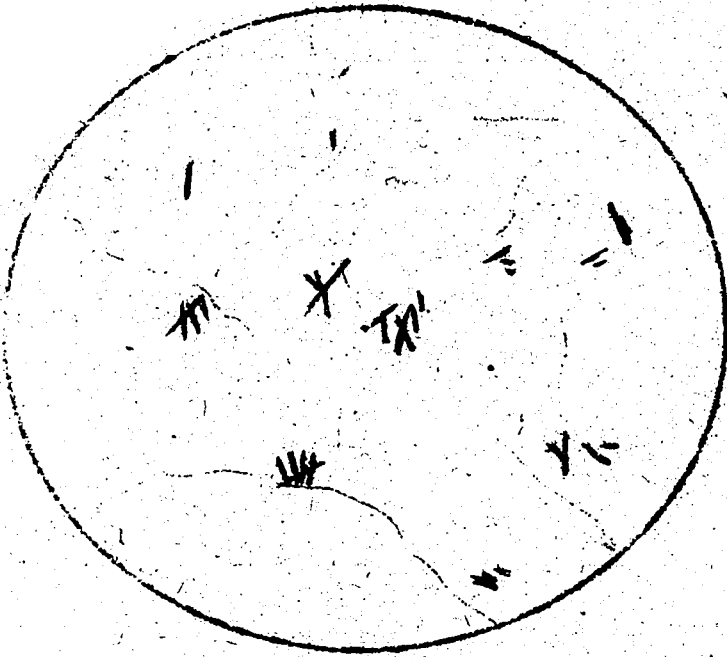
Dimensions of capillary spaces govern filtration time, and viscosity has a much smaller, but visible influence. The high molecular granular waxes go with the more viscous oils and also lead to formation of smallest filter pores. It is for both reasons that the filter cake must be kept as fluffy and spongy as possible to increase filtration velocity. That is accomplished by very moderate suction which has only linear influence upon speed of filtration and by careful avoiding of dry spots in the cake before it has been washed through properly. Wax cakes of lighter fractions naturally require much less attention in washing. Their structure is sturdier and less influenced by moderate compressing forces. Irregularities which would throw out of balance a plant operating on heavy oil may cause no harmful effect and still produce satisfactory products if a spindle oil distillate is processed. As an irreversible process compression of filter cake is evidently to be avoided for any oil.

The paraffin crystals, much in contrast to most other crystals, have no tendency to include oil or liquid. This may seem strange at first, but it can be explained by their crystalline peculiarities and the proof for it could be furnished such as follows. The question is of fundamental significance, because its answer permits at once to decide if a particular measure is suitable or not.

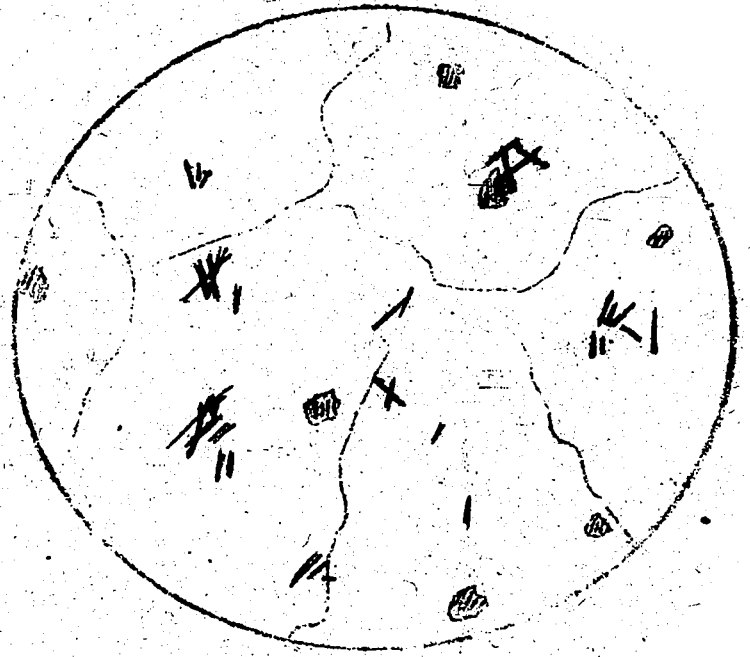
Among others it showed that from this view point there is no need for recrystallization and that repulping is just as effective. The method of testing is new and can be used with success for quick plant control as well. It is based on the addition of oil soluble dye stuffs which are readily dissolved by mineral oils, tar oils and molten paraffin. The very intense "Sudan dyes" such as

"Sudan red" and also alizarin-iriscobule oilsoluble, are very suitable, A trace of dye stuff is added to the wax which is to be investigated and it is dissolved by melting the preparation. This requires but little material and can be done on an ordinary microscope slide. The paraffin solidifies when the slide is cooled. Solid paraffin does not dissolve the above named dye stuffs and the microscopic examination will reveal that well crystallized dark dye stuff is resting besides the entirely colorless paraffin crystals. If oil is present, however, it can readily be discerned as intensely colored spots with undefined boundary, because it still keeps the dye stuff in solution. Solubility of dye in oil is limited and the addition of dye should be such as to allow some dye to crystallize. The method can be used with success to estimate the percentage of little oil in much paraffin. Oil content of 1%, 3%, and above 5% can easily be estimated, but a larger percentage than 5% will color the field of vision evenly. Naturally the paraffins to be investigated must be solid at observation temperature, Low melting soft paraffins shall be examined at lower temperature e.g. 0°C. Observation at 2 temperatures may allow conclusions how far an oil content which has been observed at higher temperature can be attributed to soft waxes. Time is of importance like in all crystallizing problems and this empirical method presumes some practice in keeping constant time between preparation of the object and microscopical examination. Five minutes or ten minutes should elapse before the result can be evaluated. The answer if a commercial paraffin is perfectly free of oil or not can be given immediately, however. Frequently there is not even need for microscopic examination, because the color shade of the dissolved dye stuff is different from that of the crystallized one. For sudan red the solution has a yellowish salmon red tint, while the crystals appear bluish fuchsia red. The test does not give conclusive results with high molecular ceresinic waxes. It works best for brown coal tar paraffin and mineral oil waxes

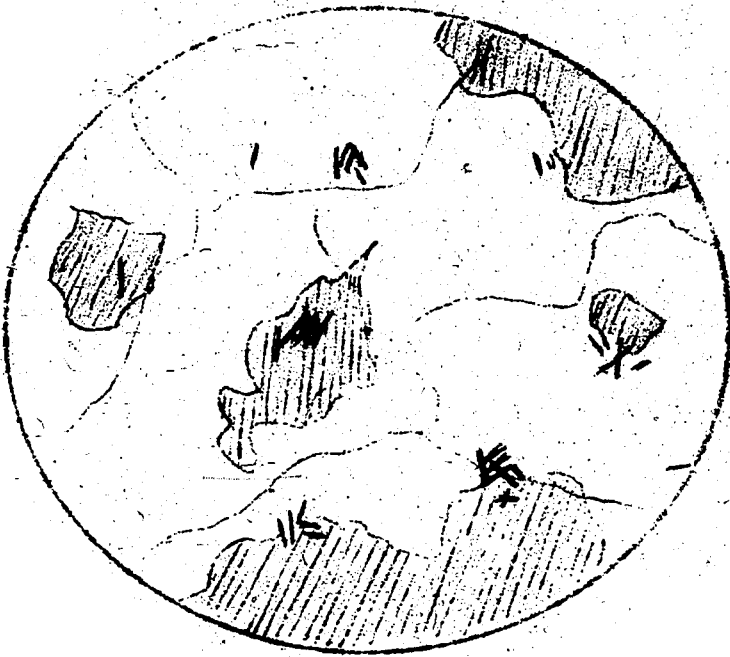
Microscopic pictures with the dye stuff test



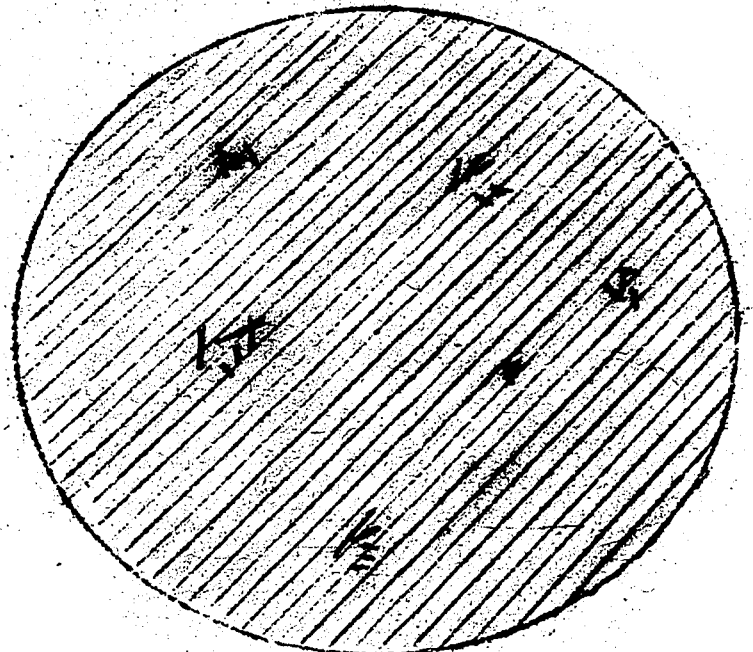
Commercial paraffin oil-free



1% oil



3% - 5% oil



more than 5% oil

of low and average molecular weight such as commercial paraffin.

If paraffin wax is separated and very well washed externally, the examination with this method will show it to be perfectly free from oil. A counter test was done by adding the dye stuff before chilling. No enclosures of dyed oil could be found in the crystals even at observation with large magnifications. It is evident therefore, that noticeable contamination of paraffin wax by enclosure of oil within the crystals need not be feared under any circumstances. A few words may be added about microscopic examination of dewaxing stocks. The objects are highly sensitive to minor addition of heat which may be caused by radiation. Only light from an artificial source, which has been well filtered through thick layers of water, should therefore be used. It may sometimes be advantageous to eliminate the red component by using monochromatic light of shorter wave length or at least to apply a green or yellow filter. The objects should be in a closed chamber. It must be able to be tempered with liquid from a thermostat and below and above the preparation there should be an insulating space which consists of two plan-parallel tightly sealed glass plates and a ring shaped groove beyond the observation field which holds a suitable desiccant. Much simpler means will suffice of course if only hard waxes are to be tested, but for comparative examination especially of soft and low melting waxes it is only by observation of all precautions, that reliable conclusions can be anticipated. Magnification need not necessarily be very high. Fifty times will frequently suffice and 500 times is seldom needed.

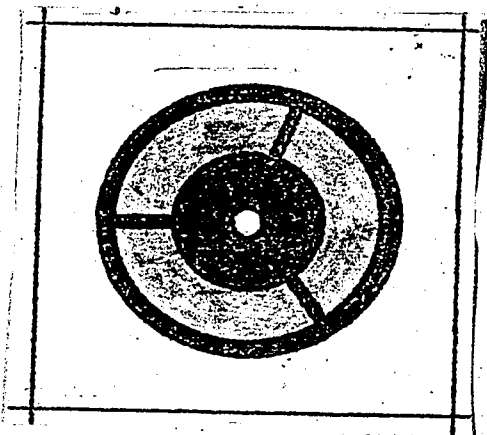
A polarizing outfit with crossed nicols and a gypsum plate is indispensable, because most examinations can only be done with polarized light. It permits conclusions about the thickness of the crystals and their optical properties and is the only reliable means to have a clear picture

~~of the crystal boundaries. The entirely different color indicates where~~
~~crystals lie above each other and continuous color change points to~~
spheric objects which may have been shaped that way by the influence of
pressure or other forces,

Dark field observation could be used very little only. It shows the
crystalline boundaries very well, but cracks in the crystals show brightly
also, and may pretend crystal boundaries.

I thought of a new way to combine the advantages of both illuminating
methods, which proved to be of value especially for the examination of very
delicate objects with poor double refractivity. A dark field diaphragm
of the usual type, which is used in combination with an ordinary condensor
to give the dark field effect is perforated in the center. The large space
for illumination are left open or better they are covered with a trans-
parent film which is colored a bright ruby red, yellow, green or blue,
depending on the object to be examined. The hole in the centre of

the diaphragm is covered with a polarizing
foil or nicol prism and the eye piece of the
microscope is equipped with a similar foil
in crossed position. A gypsum plate may also
be used, but is frequently disadvantageous
because it brightens the field of vision
evenly. It should only be used in combina-
tion with a very small central hole in the



diaphragm. This arrangement combines the use of polarized light with dark
field illumination. The central hole shall be 1, 1½ or 2 mm ϕ , or larger,
depending on source of light and object. The conical light component
can be suitably dimmed by the iris diaphragm of the illuminating outfit
of the microscope, and adapted to the polarized light component from the

central hole. This illumination shows optically active and inactive matter in different colors and underlines delicate boundaries, edges and fissures. It facilitates observation of crystal enclosures and of thin crystals with very feeble double refractivity or in extinguishing position. Evidently its use is not restricted to paraffin waxes.

Powerful condensers for conoscopic examination to show crystal axes are unnecessary, because no more conclusions could be derived from the observations than that the examined crystals were optical biaxial, which confirms former statements in literature.

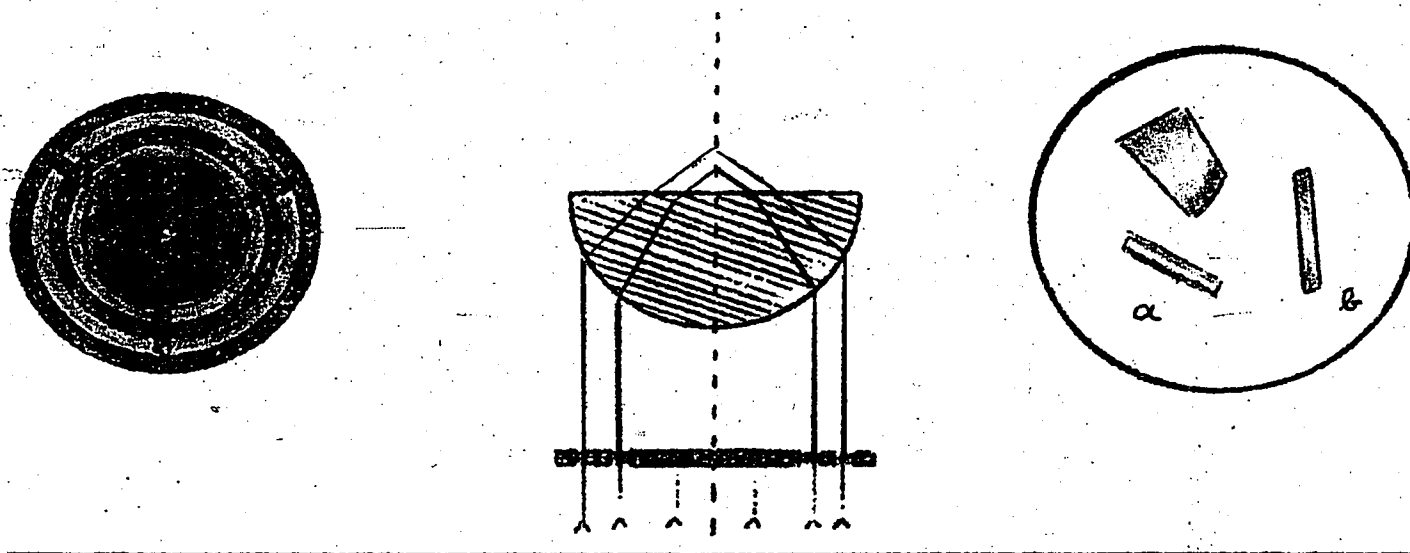
Stereoscopic attachment proved to be very useful because it gives a clear picture of crystal arrangement in space, when examining a dewaxing stock. It also is of advantage only if used with polarizing equipment. Special measures such as illumination with sloping light or light from above may facilitate examination and replace stereoscopic attachment to some extent. The test with added dye stuffs shall be done with the condenser wide open, to kill the vision of the structure of uncolored objects, the same practice which is widely used in bacteriological research. It need hardly be mentioned that all precautions must be met to avoid evaporation of solvents which would frustrate any conclusion. Photographic equipment is useful, because it permits finding out unmistakably what happened if changes occur. This all boils down to the fact that the accessories for microscopic work with paraffins are just as important as the microscope itself, but a good deal of work can also be done with improvised equipment.

Another new gadget for microscope work shall also be discussed. Although not much used for the reported work, it still widens the field of microscopic research and was occasionally advantageous in the study of wax crystals.

It also is a modified dark field diaphragm which, however, has the purpose of showing the true 3-dimensional arrangement of difficult objects

in space. Sometimes it may be more advantageous than a stereoscopic attachment and it can be particularly useful when used with it.

The idea is that focal points for different colors do not coincide for a non achromatic condenser lens. This effect is reinforced by elimination of spectral colors of white light. The dark field principle is used and the diaphragm is modified as the picture shows:



Plates observed almost edgewise appear like a) while inclined needles show like b). Evidently it will be advantageous to grind the condenser lens according to the theoretical demands. The objects must extend several $1/100$ mm in depth to show the effect. It is evident for what purposes this method will be helpful. With the available improvised equipment it worked for low magnification only.

To turn back to the dewaxing problems there remains elasticity and plasticity to be discussed. The elastic properties of paraffins are minute while the plastic ones are very pronounced. This is frequently desired and advantageous, especially so for wax coatings on soft objects, impregnation of papers etc. The more plastic coating is less likely to crack or chip off. Occasionally it is most undesired as in candles which bend and bow if made

~~average molecular paraffins. Straight chain and high molecular waxes are less~~
plastic than branched, cyclic or low molecular ones, Plasticity depends upon temperature and purity and its reduction in candle manufacturing by an admixture of stearic acid is well known. In dewaxing it is a most undesired property, because it makes the filter cake sensitive to even the slightest compressing forces and causes the crystals to change their form and to bake together. A cake which has been submitted to too high a pressure by suction or compression does not readily turn back to a spongier structure when the cause of the force is eliminated. Such a cake layer is definitely spoilt and unsuitable to give good products.

Few means only are known to counteract the influence of plasticity, because the temperature is fixed by dewaxing conditions and the addition of foreign matter is undesirable. Filtration in two steps acts favourable in that regard, although the lower plasticity of the first separating straight chain and high molecular paraffins is partly compensated for by the higher temperature of separation which also naturally increases plasticity. Lower filtration temperature is obviously useless, because it leads to the separation of soft wax constituents which make things even worse. In two stage filtration the second soft cake does not require more attention than in separation of a total wax cake, while the filtration of the first wax fraction is substantially less sensitive to all conditions which depend on plasticity, such as suction pressure, cake thickness and washing.

Filter aids like Kieselguhr or filter cel are chiefly effective by giving the plastic crystals a solid support which leads to better cake porosity. The draw back is that any added matter has to be removed again, which complicates the process.

—The best countermeasures against the disadvantageous influence of plasticity of the wax crystals are purely physical. Suction pressure shall be

kept reasonably low and the crystals must be kept well and evenly distributed in suspension. Building up of a filter cake is to be retarded as long as possible. Those demands are very closely met by the use of the below described continuous band filters and by suitable high specific gravity solvents. The high specific gravity of some chlorinated hydrocarbons as diluting agents keeps the crystals not only floating but also counteracts settling from gravity and causes them to rise gently to the surface. This does not happen in chillers, tubes or other apparatus where there is always some sort of agitation by mechanical means or turbulence. It does noticeably happen in the filter pans, where it is highly advantageous. The lower layers which are poor in paraffin content then run through the filter cloth easily and quickly, almost requiring no suction. The wax cake deposits mostly at the end of the filtration and is spongy and fluffy enough to permit easy washing with little suction. The influence of compressing forces upon the delicate system is thus reduced to the most possible minimum. Evidently it is the Buechner funnel type filter only which can accomplish that, because with heavy solvents and rotary filters the effect might be just reverse. This effect must not be confounded with the floating on top of paraffin due to the below discussed phase separation which is most harmful.

Plasticity is mostly responsible for the fact that no proper deciling can be accomplished in filter presses. The excessive pressure bakes the crystals together and seals the capillary spaces which include the oil. The size of the capillaries is furthermore greatly diminished, causing considerably higher capillary forces. Wash liquid will then pass through cracks and channels only, which makes washing ineffective. It is in analytical deciling of wax scales by pressing them between filter paper only, that oil free wax can be obtained through pressure. The pressure which then must overcome capillary and surface forces is usually hundreds of atmospheres and the thickness of the waxy layer

exceeds hardly fractions of a millimeter. No washing is possible or required. The oil content is found by solvent extraction of the oily filter paper and weighing. In large scale such a pressing process is impossible.

All commercial waxes, which have been produced in filter presses are therefore oily and must be submitted to a sweating process. Although this procedure is widely used, there seems to be no perfectly satisfactory explanation of its theory. It is reported in literature, that in recrystallization of wax from the melted press cake, the paraffin comes out in needle form. This is attributed to the lower oil content of press cakes. Needles are supposed to sweat readily. The writers explanation of sweating is as follows:

Recrystallization before sweating is necessary to open the capillaries which are obstructed and sealed in the press cake by the excessive pressure and make sweating impossible. The crystals come out in plate form, permeated with a spongy network of capillary spaces, which are now open towards the outside.

Slow rise in temperature, near to the desired melting point, has various effects. It causes the oil, which is held adsorbed and included in the capillaries to dissolve paraffin from the crystal surface and to augment its volume considerably, simultaneously widening the capillary spaces. The lowest melting waxes have obviously highest solubility and dissolve preferably.

Secondly there is also a crystalline transition. In contrast to low temperature, when wax always crystallizes in plates, there seem to be transition points at elevated temperature. This is well reflected in the curve of contraction of solidifying paraffins (See Article VII) and in the slope of the curve for transmission of polarized light through solidifying thin wax layers, (See Article VII). The curve of expansion or contraction has sharp bends at well defined temperatures. The curve of light transmission has continuous slope for slow cooling. In rapid cooling, however there is a pronounced bend

which may be attributed to a frozen-in, intermediate, crystalline state.

This seems to show that in contrast to crystallization of paraffin from solutions at low temperature, crystal habit of paraffin changes at elevated temperature, and that crystals are formed then, which are stable within narrow temperature limits only. That is not specific for hard wax, but any wax may have such transition points. The temperature of crystalline rearrangement is lower for softer waxes however and this may account for the fact that needle shaped crystals are frequently described in literature to be specific for soft wax. Unfortunately we had no microscope stage which could be heated with the required accuracy to study those crystal transitions closer.

The consequence of crystalline rearrangement of thin plates can only be a more favourable three dimensional shape, which naturally increases width of capillary spaces considerably. Height of capillary ascension is inversely proportional to capillary diameter and therefore so far decreased by rearrangement and solution that the force of gravity causes the oil to separate. That is assisted by decreased surface tension at elevated temperature and lowered viscosity. The remaining capillary forces, which would require tons of pressure to squeeze out the oil quantitatively are constantly kept balanced by a filling of the spaces with oil - oil wax solution - and finally pure wax. It is slightly lower melting and softer wax which finally remains in the capillaries, of course and this net structure can be made visible in a fresh sweated cake with the dye stuff method. (This cross section, dusted with dye powder and cautiously heated near to melting.).

Another impelling force for sweating besides gravity, is the large expansion which any paraffin exhibits when it transits from the solid state to the liquid or dissolved one. This accounts chiefly for the oil drops which are forced out of the capillary openings and show on any part of the surface of a sweating cake.

This conception of sweating explains the process quite satisfactorily and also interprets contradictory statements of crystal behaviour in literature.

The result of sweating is a perfectly oil free paraffin. This fact is another proof, that the wax crystals do not include oil or foreign matter.

The loss of paraffin in the foots oil is high, even so if a substantial part of it is recycled to sweating. Solvent filtration processes can produce the same high class waxes with much better yield and, in contrast to sweating, from any paraffinic oil or wax cake.

The capability of a wax cake to sweat depends on crystal size which spaces the capillaries, and on transition temperature of that particular paraffin. The first decreases while the latter one increases with rising molecular weight. There is evidently a limit beyond which sweating becomes impossible because the force of capillary ascension can not be reduced sufficiently. This goes together with high transition temperature of those microcrystalline waxes, the consequence of which is high solubility. Even if recrystallized these waxes will still have too small capillary spaces, but probably the crystal change to prismatic form cannot occur at all in those oily cakes because the tiny crystals dissolve and the cake melts to a slurry below transition temperature.

The capillary spaces in the high molecular wax cakes are so narrow that no oil is squeezed out by the volume increase of dissolving paraffin, but the cake expands and contracts evenly. A molecular weight of 400 - 500 is approximately the economic border line for sweating.

Evidently any process which affects crystal size favourably assists also pressing and sweating. This is known for atmospheric distillation and slight cracking of lighter cuts. No fundamental change happens to heavy and cyclic wax cuts, however, unless the wax and naturally also the oil is broken down beyond economic usefulness.

These considerations also show, that fine granular ceresinic paraffins cannot be obtained oil-free in centrifuges with any solvent. The large total

crystal surface and narrow capillaries hold much oil. The cake is unduely compressed by the gravity forces, which makes economic washing practically impossible. While centrifugal force suffices to compress the cake disadvantageously, it is not strong enough to force the wash liquid evenly through the capillary spaces. There is no chance for the oil to be replaced by solvent and while the pour point of the dewaxed oil may meet specifications perfectly well, there will always be inferior products with regard to paraffin. It is the Filtration processes only, which can turn out high class waxes plus low pouring oils for any paraffinic cut, if the theoretical demands are rigidly observed.

Filters of older design are out of question indeed. Any type of filter press is unsuitable and so are all intermittently working disc or leaf filters. The continuously working rotating disc and drum filters seem to answer the demand for a good filtration apparatus. They are much alike in their action but experiments and closer study showed that neither type was capable of serving the special task to dewax any paraffinic oil satisfactorily. A filter had to be designed on a new principle. It is known as "Continuous band filter" and it shall be discussed in a subsequent article.