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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 IV

FILTERS AND PHASE PROBLEMS

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### FILTERS AND PHASE PROBLEMS

Filtration of various waxy oils with rotary drum filters in small scale as well as in plant operation, exhibited, that efficient washing of the cake was possible in few exceptional cases only. The paraffin cakes, which deposit on the filter medium by suction are not easily penetrated. The natural consequence of the curved drum surface is that the wash liquid runs down the cake surface much quicker than it is able to penetrate through the cake. While those filters handle many porous inorganic and organic precipitates to perfect satisfaction, they are hardly capable of giving sufficiently washed waxes even from low viscous cuts.

Theoretically it is possible to reduce rotation velocity and to increase wash liquid rate so far, that any cake is given a thorough wash, but economic reasons limit those possibilities, because more wash liquid will then run down the cake surface unused, causing increased solvent recovery costs and other draw backs such as reduction of throughput and warming up of the cake.

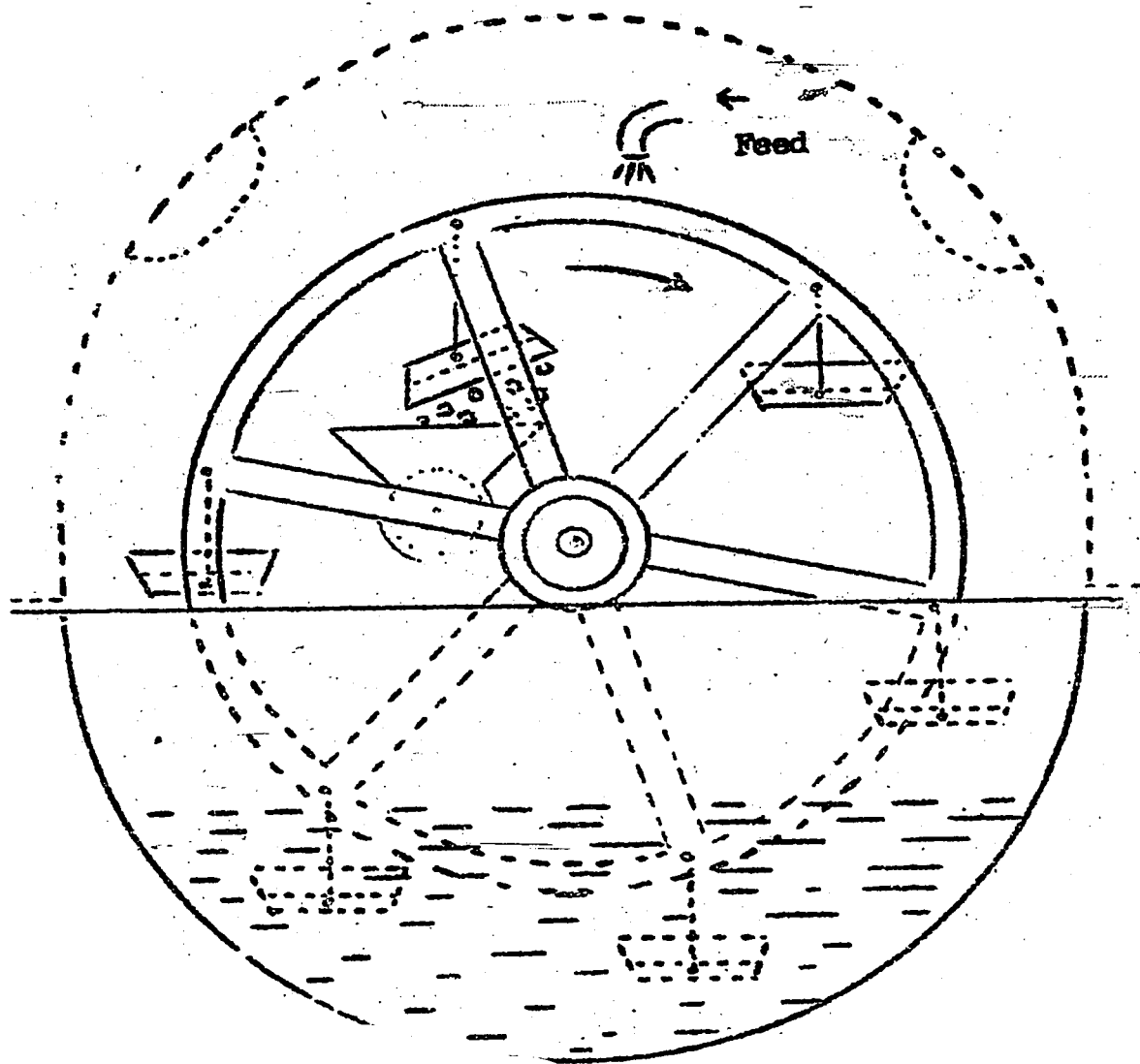
From the laboratory experiment it is evident how a technical filter should work, to be in accordance with the particular demands of dewaxing. Any wax throughout all the range of molecular weight and constitution can be obtained perfectly oil free on a Buechner funnel. Presuming that the proper solvents and dilution were chosen there was a spongy filter cake always which could be washed efficiently and exhaustively with a minimum quantity of clean wash liquid. No solvent can escape unused through side channels. These considerations led to the design of various continuously working filters of the Buechner funnel type, and finally to the band filter in which a band of many

individual filter pans permits the production of perfectly oil free waxes in a continuous process. That new type of filter is the up to the minute answer to any dewaxing problem of mineral oils and tar products and meets all theoretical considerations which should be observed in this line of manufacturing.

It cannot be denied that this type of filter is expensive, and many efforts have been made to come to simpler constructions on the same principle. One only shall be mentioned, which was developed in collaboration with the "Imperial" factory and although inferior in product quality still gave an interesting answer to the problem to design a continuously working Buechner funnel.

This filter used the idea of a Ferris wheel on which shallow filter pans were suspended. The whole system could be enclosed in a fairly small pressure shell. The lower part of the shell represented a vat which contained the wash liquid. The Ferris wheel rotated with the filter pans in horizontal position throughout the whole cycle, except one spot, where a trip turned them suddenly upside down, releasing the content of washed and dry filter cake into a hopper and conveyor. They then immediately turned back to horizontal position and were evenly fed with dewaxing stock by a rigidly coupled device which fed the individual pans intermittently. Filtration by suction happened while the pans traveled further on their cyclic way. The pan with the cake then immersed into the wash liquid, the level of which was maintained and adjusted by automatic control. There followed a drying period after the pans had emerged from the wash liquid in the course of their further cycle. The cake was discharged as described above and the pan was all set for the new cycle. Suction, pressure to blow the cake off and all other items of filtration were controlled and effected through hollow shafts and automatic valves similar in design to those of rotary filters.

Ferris Wheel Type Filter



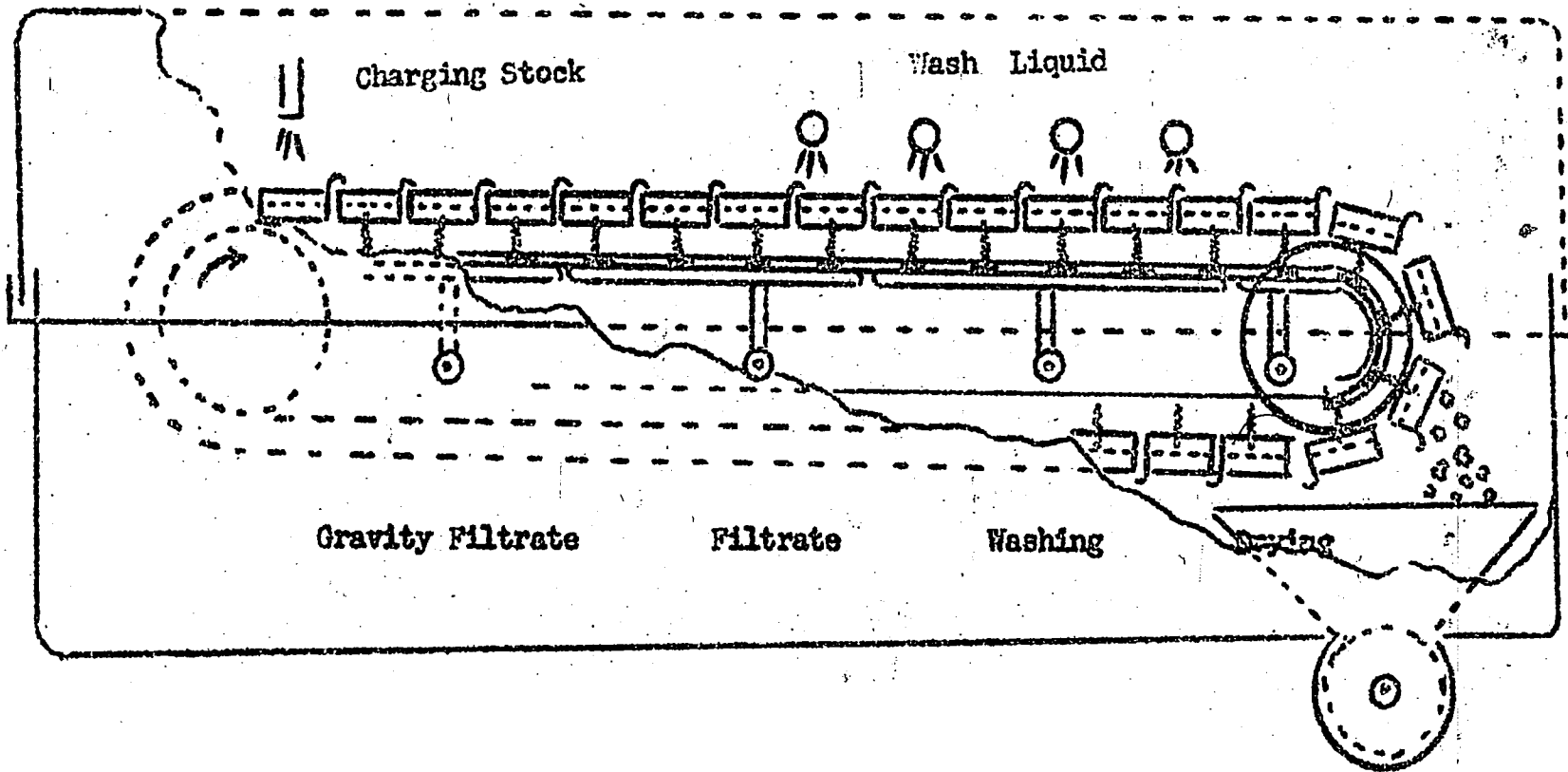
~~amazingly clever in design and smooth in operation as this Ferris wheel~~  
filter may be, it still was expensive and no satisfactory solution of the problem to separate wax cakes with optimum results. Its chief draw backs were, that the filter cake frequently got cracks and fissures before it was immersed and that the wash liquid was never perfectly clean and oil-free. Things got worse if the cake was kept wet before immersion. No cracks were then observed, but wax scales and oil was washed off the cake in the pans abundantly, contaminating the wash liquid beyond control. The authors suggestion to eliminate the solvent in the vat and to feed the pans individually with wash liquid in successive steps was unfortunately never tried out. That might still be a way to design a Ferris wheel type filter for satisfactory operation but it will further increase cost. Saving in space is considerable, however, and the arrangement makes full use of the available filter surface, in which it is definitely superior to the band filter where the pans travel back empty a long way.

Needless to say that with regard to the use of high gravity solvents this filter offers the same advantages which are typical for the band filter, to which its action is more similar than any other filtering equipment.

The described draw backs of the Ferris wheel pan filter, the difficulty in arranging intermittent feeding and emptying equipment and the wish to come to a cheaper and less complicated design caused us to develop an entirely new type of continuous pan filter in collaboration with the firm "Wolff, Buckau".

This continuous band filter met all demands in pilot plant scale and finally justified all expectations when it was installed in largest plant size. It consists basically of an endless band of filter pans which travel along a horizontal track. Then they turn upside down and travel the way back underneath. Each filter pan is connected by flexible hose with the hollow

# Continuous Band Filter



~~automatic valve rail, which is subdivided into sections and controls suction~~  
and pressure. It serves to take off various liquids from static filtration,  
suction filtration and washing, finally releasing the washed and dry filter  
cake by a pressure impulse. No complicated gadgets are required to feed, wax  
bearing oil and wash liquid, which are simply admitted continuously through  
ordinary valves and distributed evenly over the filter pans by notched grooves.  
Besides the rotating wheels which propel the conveyor chain for the pans, and  
the screw conveyor for discharge of the filter cake from a hopper and vat at  
the bottom of the shell, there are only sliding assemblies of simple design  
and rugged construction, which are most unlikely to fail in service. All  
important factors for filtration are constantly under control and any adjust-  
ment can be made at any time. Such adjustments pertain chiefly to filter  
cake thickness, number of steps in washing, quantity of wash liquid, vacuum  
for filtration, time for drying and pressure to blow the cake off. Any wax  
bearing oil can be handled, and it takes but little time to switch from one  
oil to another. That flexibility and the perfect theoretical presumptions  
for wax filtration justify an extensive use of this filter for dewaxing, in  
spite of the above mentioned disadvantage that only part of the filter sur-  
face is actually in service for filtration and that it is rather bulky.

That filter has been described in detail by J. P. Jones in Nat. Petr.  
News, May 1, 1946 (Vol. 38, No. 13) and no additional explanations are nec-  
essary. The writer's ideas for simplifications and further improvements of  
band filters was halted in the experimental stage.

It is natural that engineering science will further improve that type  
of filter from mechanical view points. It may be simplified and made cheaper.  
The principle of a continuous Buchner funnel must be maintained, however,

because it is the only perfect answer to all demands of theory and the one which turns out low pouring oils and simultaneously oil free wax cakes in a single cycle. The use of suitable solvents and observation of the phase rule laws, which are dealt with below, is imperative of course, because such filters cannot perform miracles either.

### Solvents and Phase Rule

An oil which is to be dewaxed requires dilution with a low viscous solvent. Such solvent serves to break down viscosity such as to make possible decent heat transfer in chilling, good filtration rates and suitable crystalline structure of the wax. The use of low boiling mineral oil fractions for dilution had its main draw-back in the high solubility of paraffin in those cuts. The disadvantage of high inflammability could be eliminated by such precautions as inert cover gas, but solubility cost the refiners hard cash, because it made it necessary to chill to much lower temperature than to the required pour point, and refrigeration is very expensive. In the following hunt for a good solvent it was some chlorinated hydrocarbons and binary solvent mixtures which finally proved most satisfactory. The chlorinated hydrocarbons offered advantages in centrifuge design due to their high specific gravity and in solvent combinations it was benzol-acetone which became leading for filtration processes because it could be adapted to the charging stocks by alteration of the percentage of its components. Table on next page gives solubility at  $-20^{\circ} \text{C}$  of paraffins in some solvents.

In selecting a suitable solvent it is not solubility of wax in it only which has to be considered, but numerous other demands must be met as well. The price must be low for economical reasons, because no recovery system works without loss. That is why some fluorinated hydrocarbons could not be



g/100cc

Solubility of paraffins in solvents at -20°C

Melt.P. 43,5°C

Melt.P. 60°C

Melt.P. 61,5°C

WAX FROM SPINDLE OIL

WAX FROM LUBRICATING OIL

WAX FROM PROPANE DEASPHALIZED RESIDUE

GASOLINE  
BENZENE - TOLUENE (50:50)  
C<sub>2</sub>H<sub>4</sub>(C<sub>2</sub> - GASOLINE (65:35)  
BENZENE - ACETONE (75:25)  
DICHLOROMETHANE  
BENZENE - SO<sub>2</sub> (75:25)  
CH<sub>2</sub>Cl<sub>2</sub> - C<sub>2</sub>H<sub>4</sub> (50:50)  
PYRIDINE  
DICHLOROETHANE  
BENZENE - SO<sub>2</sub> (25:75)  
ACETONE  
SO<sub>2</sub>

suggested for technical use, although their properties as dewaxing solvents were close to perfect. It is stability to hydrolytic influences and to thermal decomposition furthermore, which is important. The solvent must be evaporated and recovered by condensation. Products of decomposition or oxidation are usually corrosive and must be avoided by all means. Obviously the diluting agent itself must not have corrosive properties either, for the use of special alloys would make plants too expensive and a dewaxing plant is costly anyway. Some moisture is always carried into the plant with the charging stock. Therefore, drying of the solvent should offer no difficult problems. If a mixture of two solvents is used there must be an easy way available to measure the percentage of each component and the recovery system must necessarily permit to recover the components separately. The engineer wants the solvent to have favourable caloric data to keep the operating costs low. Finally the solvent should have a low boiling point in order to keep temperature low in recovery and to permit the wax and the oil to be perfectly freed from it. Health regulations ask for a non-poisonous chemical and safety reasons for a non-inflammable one. Naturally it shall have a low viscosity, because breaking viscosity is its main job. This evidently limits the number of suitable solvents considerably and they are even more reduced when the problem of miscibility and phase rule laws are considered. It is the mixture of benzol-acetone, benzol-sulphurdioxide, and of some chlorinated hydrocarbons only which besides propane as a single solvent are of technical importance presently.

Dewaxing processes, working with ester mixtures and single solvents still exist in a few small units in Europe, but the results are poor and those processes will become obsolete.

The use of propane was the first advance which was made to link two different technical processes which were based on the same solvent. Propane had some draw-backs of course because its solvent power for paraffin was substantial even at low temperature, although it was lower than that of higher aliphatics. It was highly inflammable and had high vapor pressure, requiring special safety precautions. But it seemed to have perfect miscibility with all sorts of mineral oils, its heat of evaporation could be utilized for chilling and the combination with a deasphaltizing unit gave economical advantages which compensated partly the refrigerating effort that had to be made in order to get decent pour points for solubility reasons.

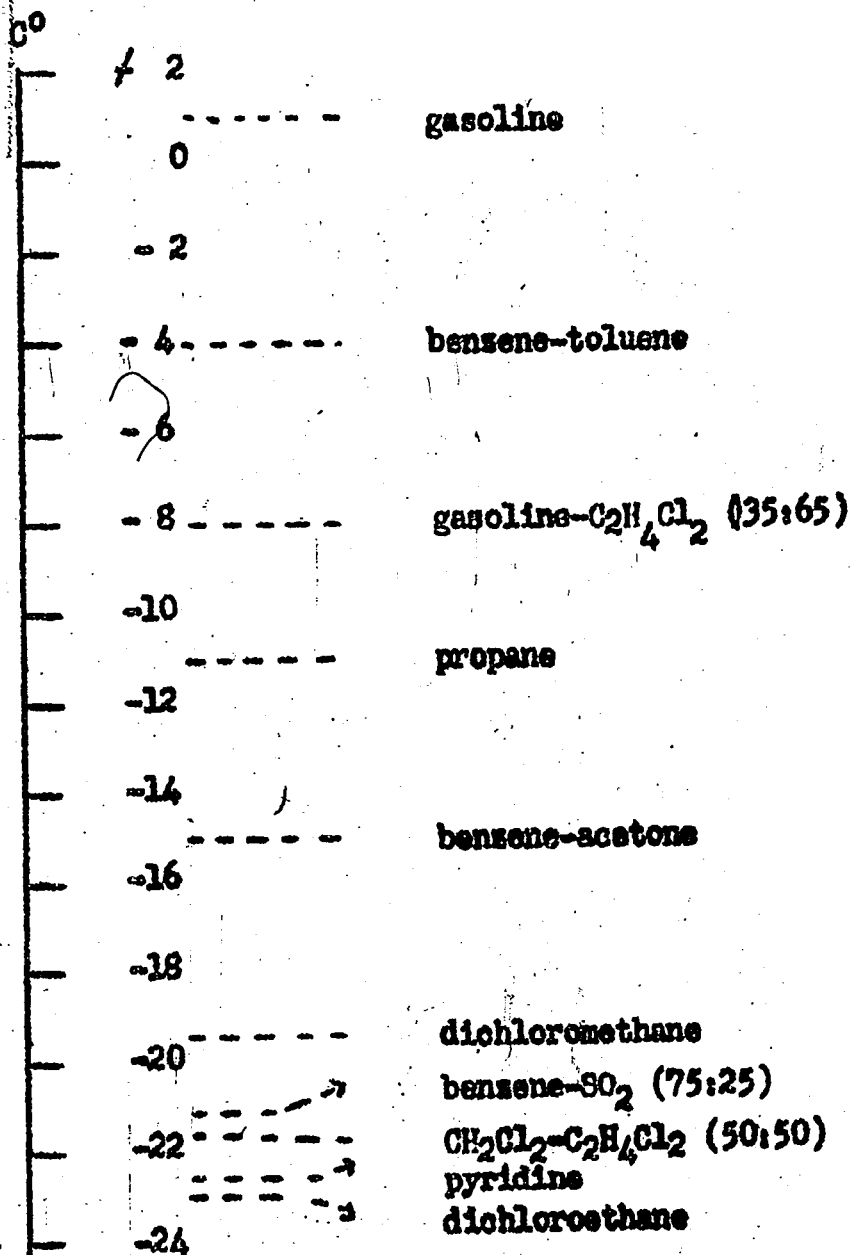
The first double solvent was benzol-acetone. It was a dewaxing agent only, with high flexibility and its introduction meant a considerable progress. A new solvent combination came up as a competitor about the same time, which could tackle the same problems but had the advantage to be capable of being used as a refining agent and refrigerant as well. This was the combination of benzol with sulphurdioxide which could serve for refining an oil by solvent extraction first and for dewaxing it afterwards with the solvent components blended in reverse proportion. The economic advantages of the so-called Edeleanu process for refining were known and the new combination offered a saving with regard to solvent recovery. The combined plant based on the same solvents could be designed cheaper and use of benzol-SO<sub>2</sub> for refining, dewaxing and chilling simplified the question of storing the solvents. The danger of inflammability of benzol was substantially lowered by the addition of the non-combustible sulphurdioxide. With regard to corrosion it offered no new problems, and the old ones which had been formerly encountered when SO<sub>2</sub> was used in presence of moisture had been perfectly overcome. The nasty smell of SO<sub>2</sub> also had an

~~advantage, because it indicated small leaks and that is why those plants~~  
could be operated with a minimum loss of solvent. Solvent power for paraffins especially for high molecular ones was trivial. (See next page).

The problem of phase separation did not exist when the oil was diluted with low boiling fractions from mineral oil, because they were readily miscible with the charging stock in any proportion. The new solvents were aliens to oil, however, and while they answered the demand for low solubility of wax, they brought about new difficulties which were fully recognized in recent times only. With regard to wax removal they gave good results and the pour points which could be obtained did not fulfill all expectations only but surprisingly they could be below dewaxing temperature. But then the oil had suffered a decrease of quality, and the worst of all was, that the wax cakes held back a high percentage of oil. Analysis showed that this oil had frequently higher quality than the dewaxed stock and the oil content did not mean a contamination of the paraffin only, but the loss of most valuable oil components as well.

The study of phase rule disclosed the way to avoid all difficulties and explained what had happened before. Low solvent power of diluting agents for wax controls only partly the pour point of the dewaxed oils, but the strict observation of miscibility, is decisive for the quality of the wax of the oil and for a multitude of technical figures of which only filtration rate shall be mentioned. The study of phase equilibria is the dominating demand in the art of dewaxing.

Pour Point

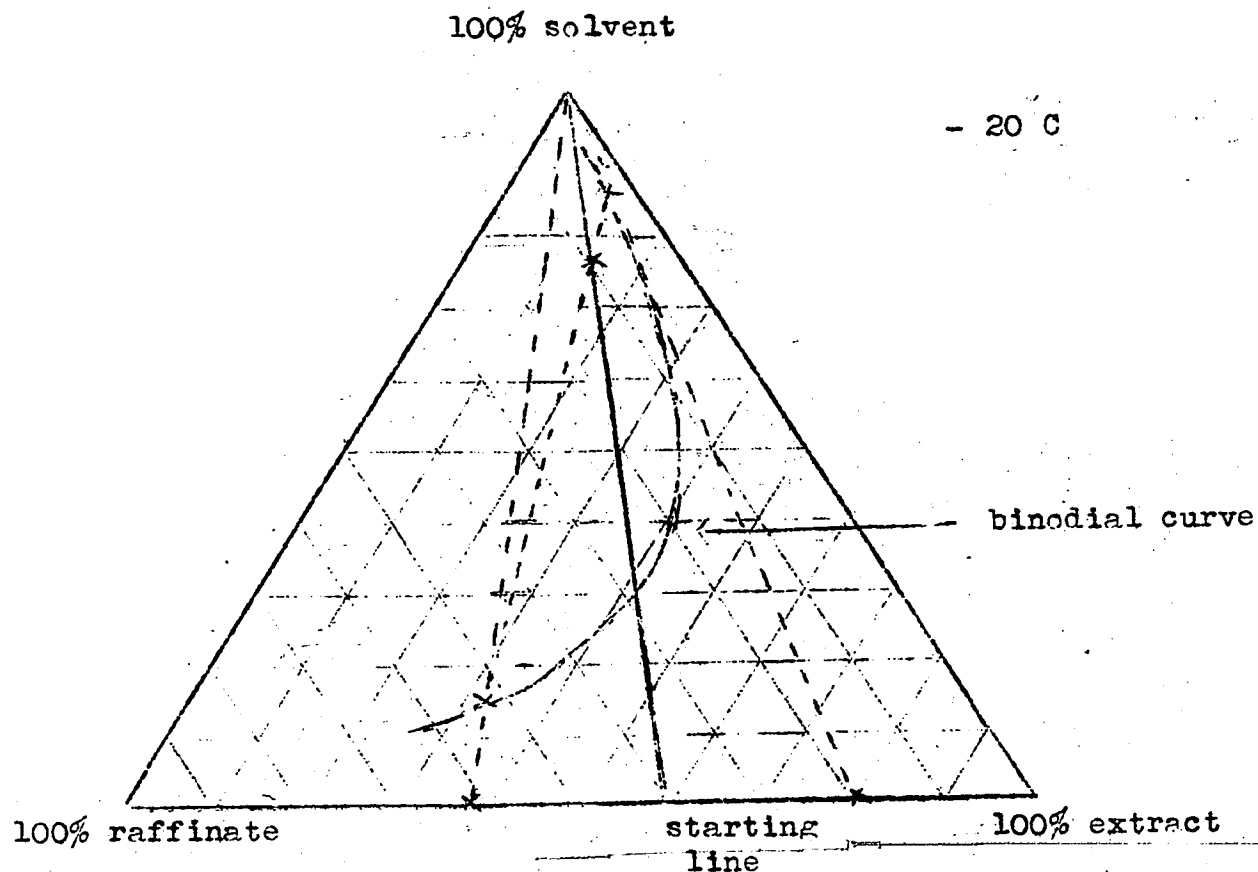


Rise in pour point is caused by the solubility of paraffin in various solvents. The figures refer to 400% solvent consumption in experimental dewaxing of a heavy lub. distillate at -24°C.

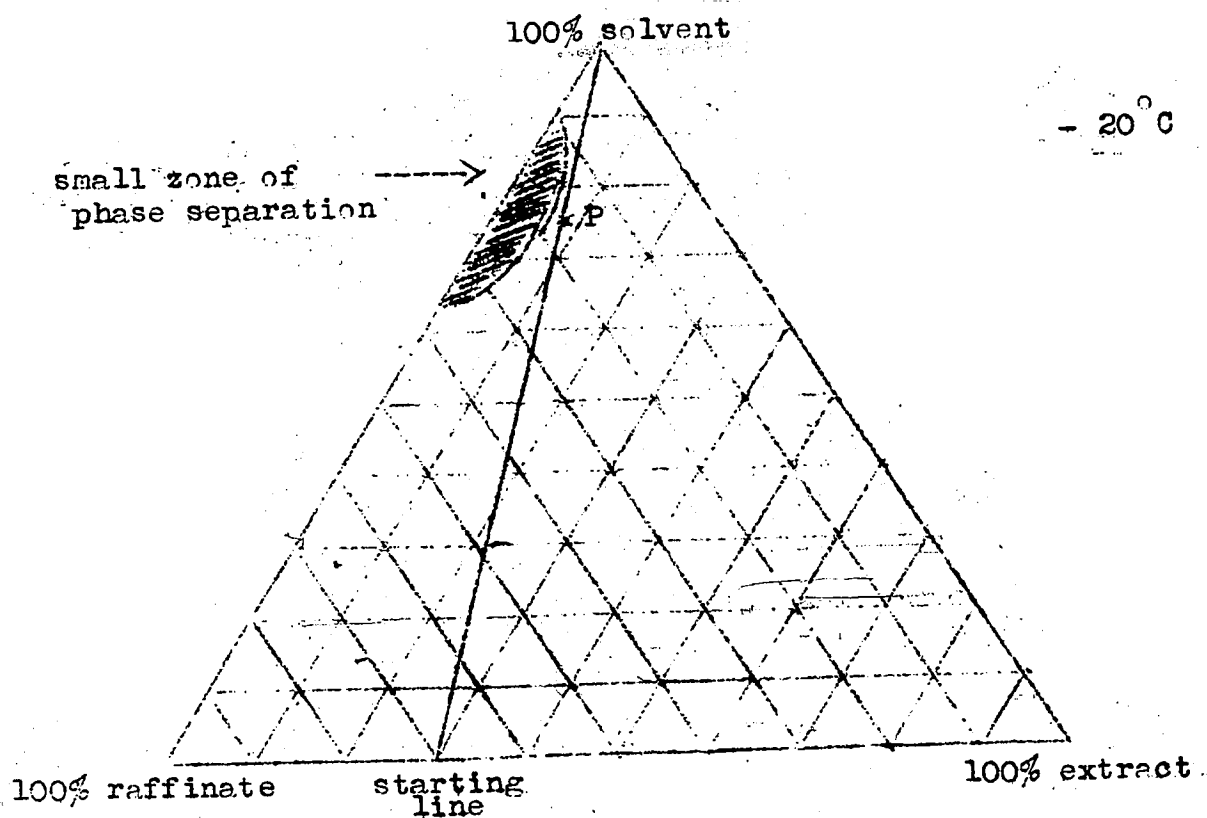
## The triangular graphs

A system of multiple components which are not miscible in all proportions can disclose most of its secrets if the line of phase separation is plotted as a so-called binodial curve. No solvent refining can be done successfully, unless refining conditions are adjusted in accordance with the conclusions which can be derived from the triangular graphs. The theoretical principles were first transferred to refining of mineral oil products by Hunter and Nash and critically studied by Van Dijck and collaborators. They are widely known and shall be mentioned briefly only. The three corners of a triangle represent 100% of a pure component. Oil is a mixture of many chemical individuals, indeed, but it may as well be considered as a binary system of saturated compounds of high stability, and unsaturated ones, with poor viscosity curves and lubricating properties. The first group we call raffinate, the latter one extract. They are the left and right corners in the base of our triangle. The apex of the triangle represents 100% of pure solvent, which has been suitably selected with regard to poor solvent power for paraffin. The paraffin wax itself need not be considered. It exists in the form of a solid precipitate only, in which the other components are saturated, and the quantity of which is therefore without an influence upon phase equilibrium, as it is known. Temperature is of great influence and a curve can be drawn for one well defined temperature only. That means, that each binodial curve is necessarily an isotherme. It is only a few lines, which are interesting for dewaxing, much in contrast to solvent refining. This is the boundary line which separates the field of complete miscibility from the field of phase separation and the so-called starting line, which is given by the character of the oil and runs from the solvent vertex down to that point

of the triangle's base which represents the composition of the oil. It may be specific gravity or viscosity-gravity constant which are plotted there. Each oil has to be dealt with individually of course. Solubility does not depend on the proportion of saturated or unsaturated compounds only, but on molecular weight as well and the boundary curve of miscibility runs differently for lower boiling mineral oil fractions and for high boiling ones, even so, if their chemical character should happen to be the same. Another line, which requires to be mentioned, connects the points which represent the composition of the raffinate and extract solution when phase separation occurs at a certain percentage of dilution with solvent. These tie lines are of importance for solvent refining. For dewaxing it is the two ends only, which interest us, because the straight line, which may be drawn through them and the top of the triangle cut the base line and indicate the quality of the oil which eventually has been knocked out, and its percentage.



The solvent need not be a chemical individual. On the contrary it proved to be advantageous to use a combination of two solvents which could be adapted to any oil with regard to solubility of wax and optimum triangular considerations. Besides the chemical character of an oil and its molecular weight, it is the percentage of dilution which is of deciding influence upon phase separation. The desirable condition for feeding stock to the filters is expressed in the following graph:



There should exist a small zone of phase separation for the more saturated components of the oil. That does not mean that the oil will give phases when diluted, but its more valuable constituents shall not be readily miscible with the solvent under all circumstances.



The starting line will move to the right for distillates and the solvent must then be readjusted such as to give a larger zone of non-miscibility. In our example on the preceding page a preredefined oil is diluted with 300% of solvent. Point "P" in the diagram indicates the composition of the mixture. This point should be close to the boundary curve because that gives an allowance to minor fluctuations in dilution rate and temperature without the danger of phase separation and experiments show that most favourable data are obtained in this case. It is obvious, that the demand for such a flexibility can never be met by a single solvent and that the use of blended solvents is a must for optimum results. A single solvent can only be perfect for one special grade of oil or for one special boiling range. It lacks, however, flexibility with regard to the treatment of any sort of oil. It will be fully unsuitable for refined oils if it were good for distillates and it would give poorer technical and chemical data with light lub oil fractions if it were capable of dewaxing heavy cylinder stocks. Always seen from the view point of optimum results at constant temperature for dewaxed oil and paraffin. This is another reason why the modern dewaxing processes are superior to older ones which worked with single diluting agents.

The slope of the binodial curve is naturally different for various solvents. Phase separation means, that the oil which has separated is very different in quality from the charging stock. However small or large its quantity may be, it has highly saturated character and the starting line will shift for that oil far to the left. That means, that its solubility in the solvent is very limited, and it is one reason why it is practically impossible to wash a wax cake oil-free if phase separation has occurred to the dewaxing stock unless washing is done with another solvent of entirely different selectivity.

It is possible to choose solvents for which the binodial curve has  
favourable slope and for which the tie lines run almost vertically.

Phase separation will evidently be disadvantageous in this case also, but the oil which separates is not much different from the charging stock, and its removal from the wax cake by washing is easier. Some chlorinated hydrocarbons belong to that group of solvents. Efforts must be made in any case to avoid phase separation, because if it occurs there are not minor traces of oil, which separate, but the quantity of oil referring to contamination of the wax cake is considerable and may fluctuate between 5 and 50% depending on the solvent and oil and on the conditions of dilution and chilling. Triangular graphs give abundant information about miscibility problems, but it is a tedious and time consuming job to get the experimental support for a binodial curve, and one which requires highest experimental accuracy. The worst of it is, that a new curve must be drawn for each single temperature, for each boiling range and for each grade of oil. Satisfactory information and some important data, which the binodial curve does not supply, can be obtained more rapidly.

We know, that 200% - 400% dilution is required to break viscosity and only this range need to be considered. A small quantity of dewaxed oil can quickly be prepared from the oil which is to be investigated with any suitable solvent in the laboratory. That oil is then diluted with various percentages of the solvent, which we want to use, and the mixtures are slowly and cautiously chilled in test tubes. The temperature when phase separation occurs can readily be seen by a breakdown into phases, or for dark colored oils by the formation of a turbid emulsion. This is done for different dilutions, different solvents and different oils and we can easily select the most suitable dewaxing conditions.

~~This way is simple and answers the question for the basic presumptions~~  
of the production of oil-free wax from a given oil. Some experts have formerly suggested to simply check the melting point of the wax for indication of phase separation. The graph on the following page shows that this method is not reliable. Accurate determination of melting points within fractions of a degree requires much attention and the depression of the melting point by oil is not large. Standard samples of oil free wax must be made which is a possible source of error. It seems hopeless to detect very little oil in wax with this method.

Wax traces in the dewaxed oil, on the contrary show very well and graph on page 80 gives the increase in pour point, which is caused by dilution with 40% solvent, for the reason of solubility of paraffin in solvent.

It was stated above, that the dewaxing solvent shall be a binary mixture of which one component is readily miscible with the oil over a wide range of temperature and dilution, while the other one has narrower limits of miscibility. Limited miscibility may result for three reasons that is;

selectivity to molecular weight (high - low, e. g. nitrobenzene)

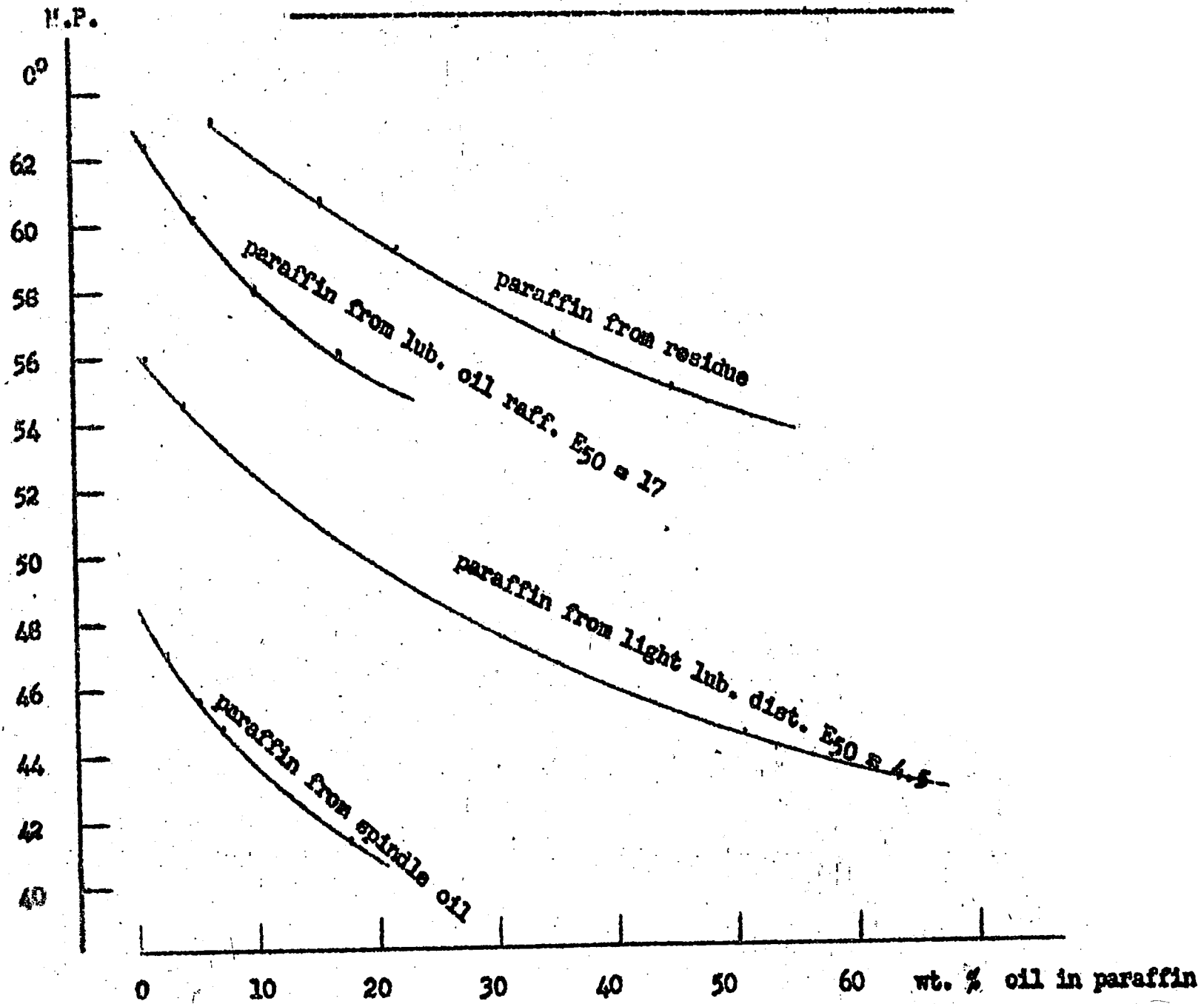
selectivity to constitution (straight - branched - cyclic, e. g.

$C_2H_4Cl_2$ )

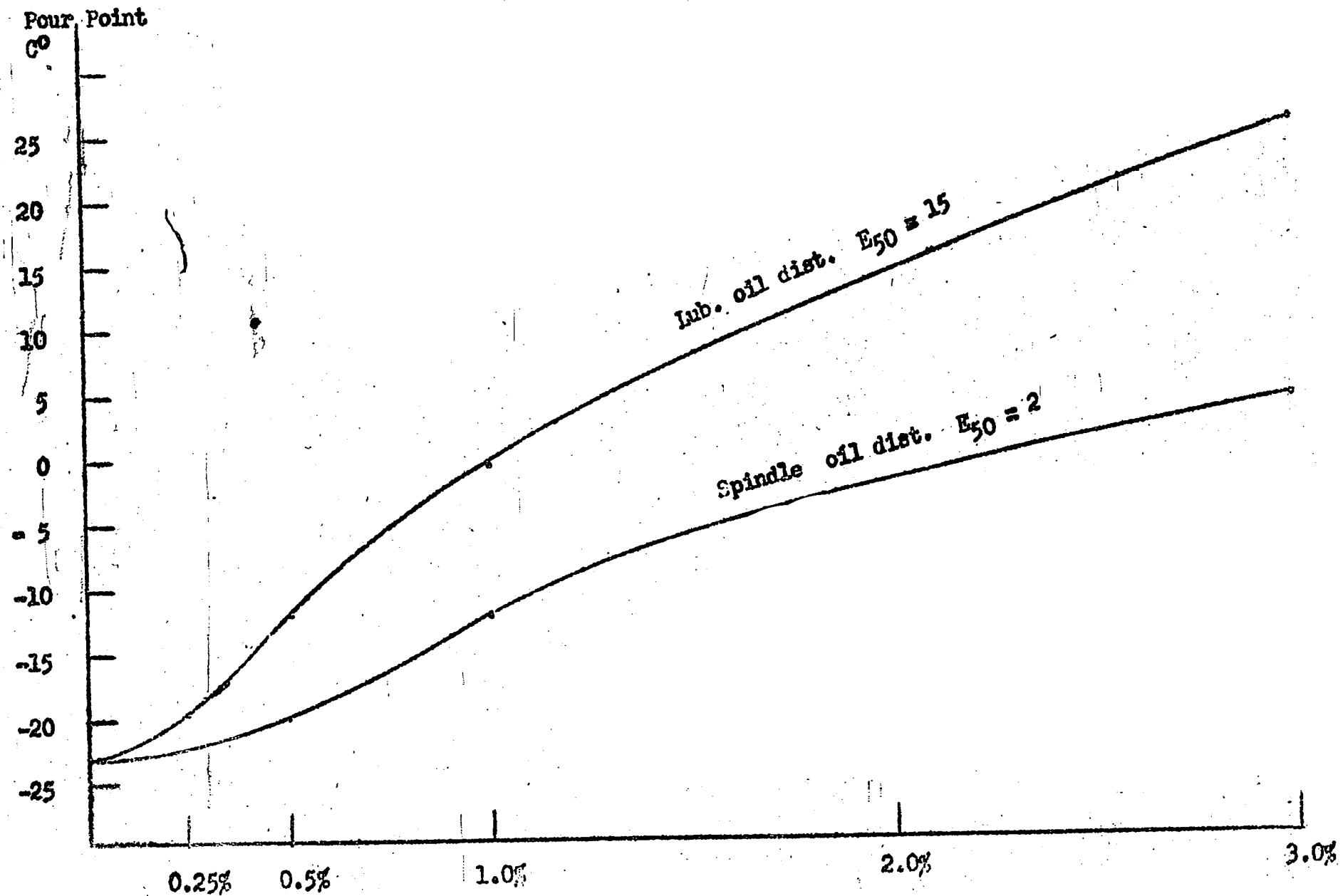
selectivity to character (saturated-unsaturated, e. g. sulfur-dioxide)

It seems not possible to find a commercial solvent which has only one of those selective properties; they usually go together but one sort of selectivity prevails, depending upon experimental conditions. It is evidently important to select for dewaxing, solvents which are little sensitive to chemical character and molecular weight, while they shall respond to chemical constitution.

Melting point depression of paraffins by oil content



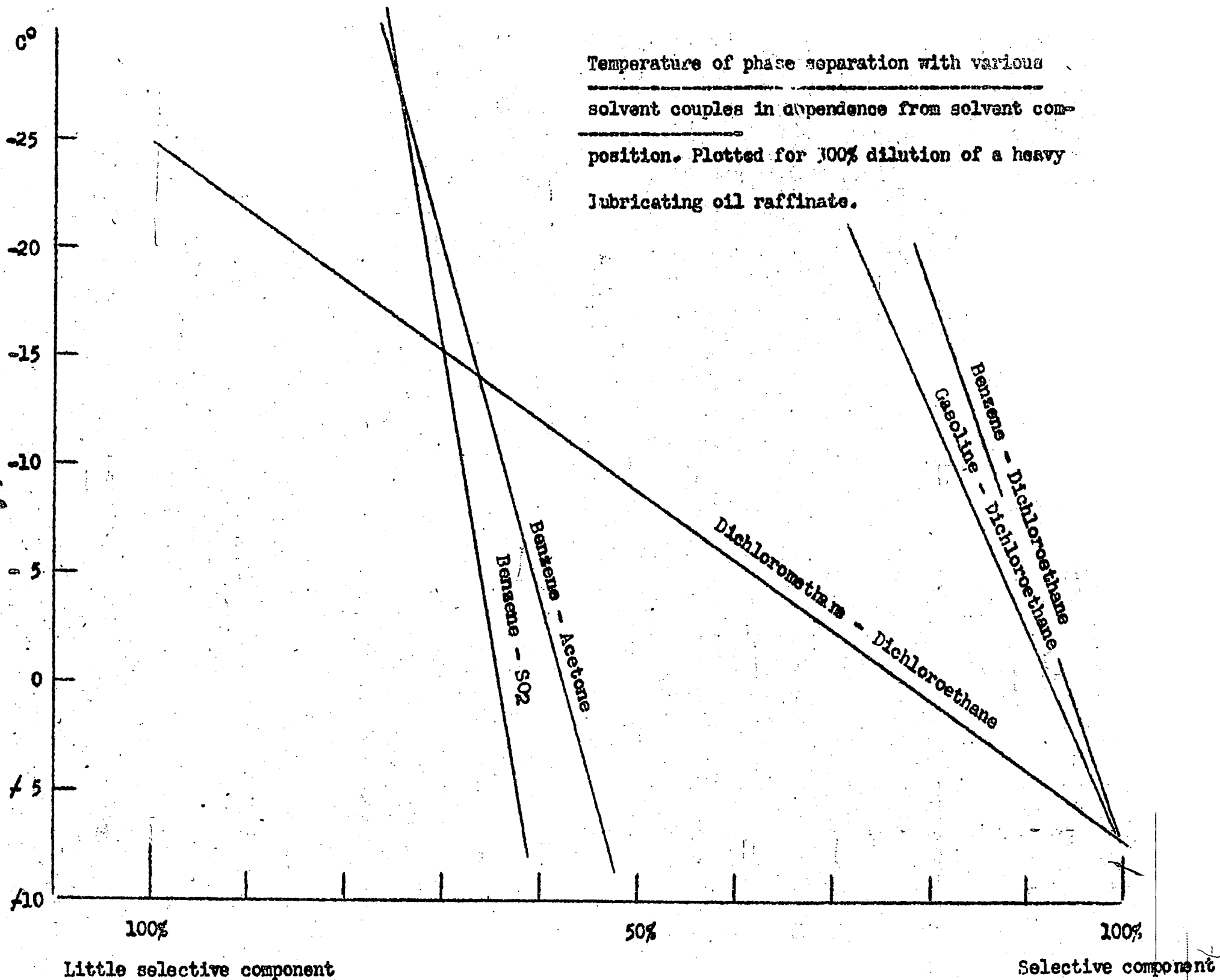
Rise in pour point for gradual addition of original paraffin  
to dewaxed oils



Selectivity shows in the breakdown of a homogeneous solution into phases at a well defined temperature which depends on solvent, oil and solution. It is expected that mixed solvents give the plants flexibility by allowing a wide margin in the blending ratio of the components. That can be accomplished if the solvent couple is not the combination of a very selective agent with a practically non selective one, but if both components have more or less moderate selectivity of their own. Water, for example, is highly selective and does not dissolve any oil at all and pyridine dissolves oil well and blends readily with water in all proportions and the mixture with little water is a dewaxing solvent which can give very good results. Still the combination pyridine-water would be unsuitable just from the view point of flexibility. Minor changes in water content of a fraction of one per cent will cause a big change in selectivity. The graph on page 81 exhibits the lines of phase separation at 300% dilution of a heavy oil with some important solvent combinations in dependence from the blending ratio of the components. These are benzol - acetone and benzol - SO<sub>2</sub> which both belong to the older type of successful solvents which are still now in use, and the chlorinated hydrocarbons dichloromethane - dichloroethane which recent research proved to be superior to other solvent couples which found their way to large scale dewaxing units.

Sulphurdioxide and acetone are known to be very selective agents. The first one found ample use for solvent refining of mineral oil fractions and its selectivity was so considerable, that it had to be decreased for the treatment of heavier cuts by elevation of temperature or blending with non selective chemicals such as benzol. Acetone had been used for analytical separation of mineral oils and isolation of their components by solvent extraction. The blend with benzol as non selective component was a satisfactory answer to the refiners demand for a good dewaxing agent. However, we learn from the curves

Temperature of phase separation with various solvent couples in dependence from solvent composition. Plotted for 300% dilution of a heavy lubricating oil raffinate.



for benzol-acetone and benzol-SO<sub>2</sub> that it takes but small changes in the proportion of the components to shift considerably the temperature at which phase separation occurs. SO<sub>2</sub> is more selective than acetone but even with acetone will the temperature of separation into component parts slide up eight centigrades, when acetone percentage increases 5% only. Blending ratio in plants must be watched carefully or the products will be unsatisfactory, chiefly with regard to the wax cake, of course. The easier adjustment of SO<sub>2</sub>-percentage compensates partly for the steeper curve in Benzol-SO<sub>2</sub> plants, and both solvents have proved to be able to give identical results in large scale.

The progress which has been reached by the dichloromethane-dichloroethane combination is evident from the graphs. It is not only the lower solving power for paraffin which makes that chlorinated solvent advisable. The slope of the curve of phase separation indicates the large reserve and flexibility which is hidden in component ratio. It is a change of 25% in contrast to 5% which will shift temperature of phase separation eight centigrades. That is a safety factor of importance. It also makes possible to give up careful fractionation in the solvent recovery system because the components need not be recovered in high purity. Machinery is simplified and treating costs are cut down.

An interesting observation shall be mentioned here. Some experiments were done with a blend of gasoline and dichloroethane to study the influences of a component in which wax is very soluble. Although this mixture is to be discarded for general use it seemed to indicate that the low mineral oil fractions have a hidden selectivity to higher molecular constituents of petroleum oils, because a larger percentage of gasoline than of benzene is required in mixtures with dichloroethane to give the same depression of miscibility temperature. That selectivity will be more pronounced for the lower aliphatic hydrocarbons, and last but not least that may be one reason, why wax cakes from heavy cuts were always oily if they were obtained with low molecular aliphatic solvents.

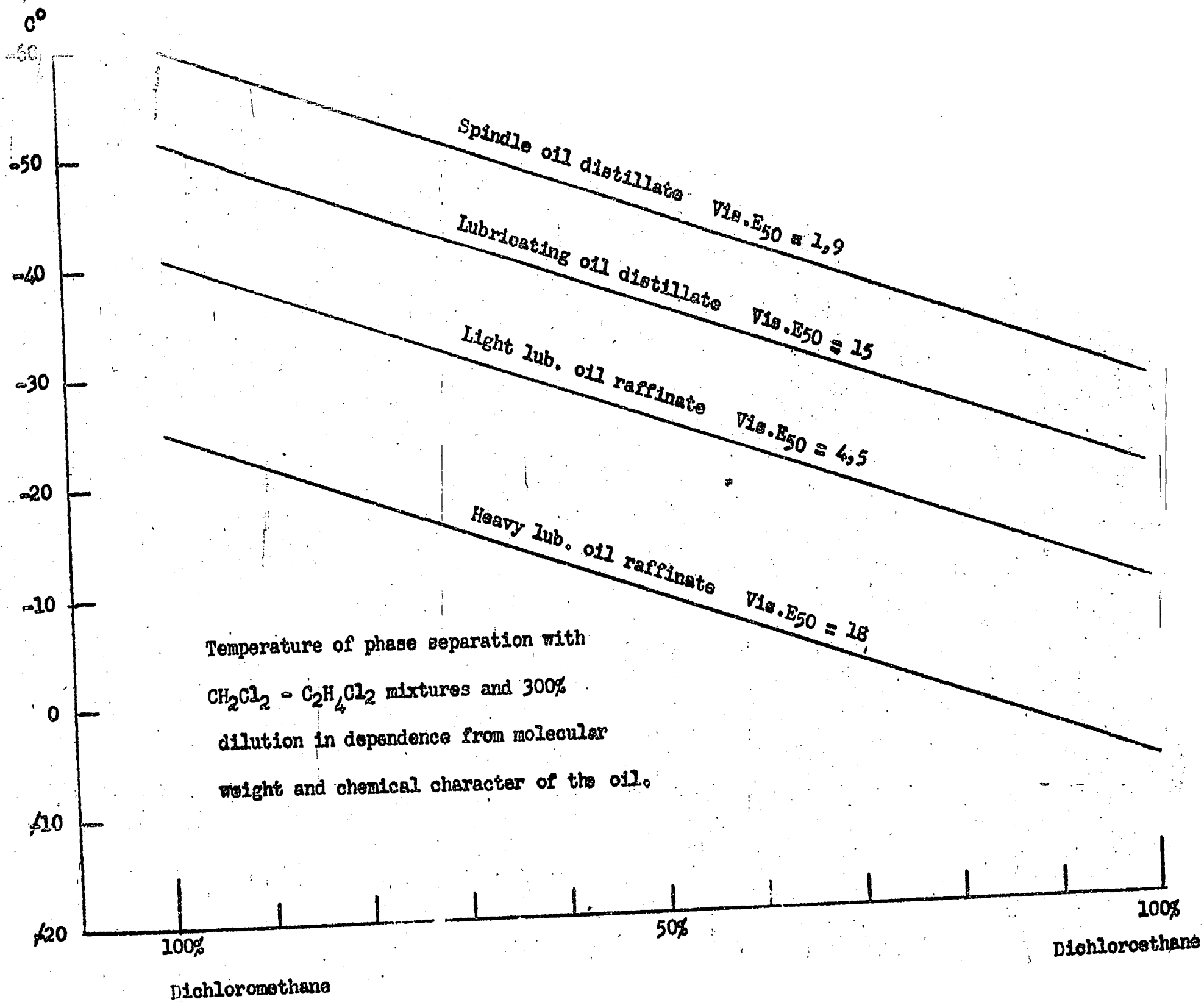


That hidden selectivity is the reason why gasoline knocks hard asphalt out of residual oils and why the lower boiling and more selective propane is able to precipitate hard asphalt, soft asphalt and high molecular resins from distillation bottoms. Propane has been found suitable for deasphaltizing empirically only and some day it will be replaced by a better solvent. The described simple miscibility tests may be helpful in finding other suitable asphalt precipitants.

The selective properties of propane and low aliphatics will then find another field of industrial application until better agents will replace them there also.

The influence of molecular weight and chemical character upon temperature of phase separation is shown for  $\text{CH}_2\text{Cl}_2 - \text{C}_2\text{H}_4\text{Cl}_2$  on page 84. Temperature of miscibility limits is generally higher for increasing molecular weight, as well as for more saturated chemical character. That holds true for any oil and any solvent blending ratio. The influence of chemical character seems to be preponderant.

Many experimental filtrations have been done to obtain information about the changes of important characteristics in dependence from dewaxing conditions. Homogeneous and heterogeneous systems were studied and the conditions were chosen such as to show differences as plainly as possible, but not <sup>to</sup> demonstrate large plant efficiency. Refining for instance was always done in batches and the yields which were obtained were comparable among each other indeed, but they were naturally different from results which can be obtained in commercial factories under perfect conditions such as continuous counter current flow, temperature gradient etc. Traces of wax were left in experimentally predewaxed stocks on purpose, to make the effect of after-refining on pour point more evident. Dewaxing was done in the laboratory with small filters which exhibit the influence of varied conditions upon physical and chemical data and upon filtration rate, calculated in kilos per square meter per hour. For conclusions



as to filter rates of large units they are of limited value only. Thick and heavy filter cloth was taken in some cases where only slight differences in the results could be expected and filtration rate depends considerably on the type of filter cloth.

Two of those experimental series shall be reported. They reflect the behaviour of a very viscous, solvent refined paraffinic distillate from Austrian crude with the important solvent couple Benzol Acetone and with dichloromethane which for such a high molecular raffinate is suitably used without addition of dichloroethane. (See pages 87 - 88).

The following results can be read from the curves for either solvent:

1) The line of phase separation must not be trespassed under any circumstances. It is only filtration rate which then grows rapidly, while all other data are changed most unfavourably. Quality of oil and wax decrease with a sudden leap and the lower pour point of the oil is paid high with a substantial decrease of viscosity index.

2) In the homogeneous field it is desirable to come close to the temperature of phase separation for the following reasons:

a) Pour points of dewaxed oil are then substantially lower because wax is less soluble in solvent.

b) The oils have maximum viscosity for the coordinated V. I.

3) It is undesirable to approach the line of phase separation because

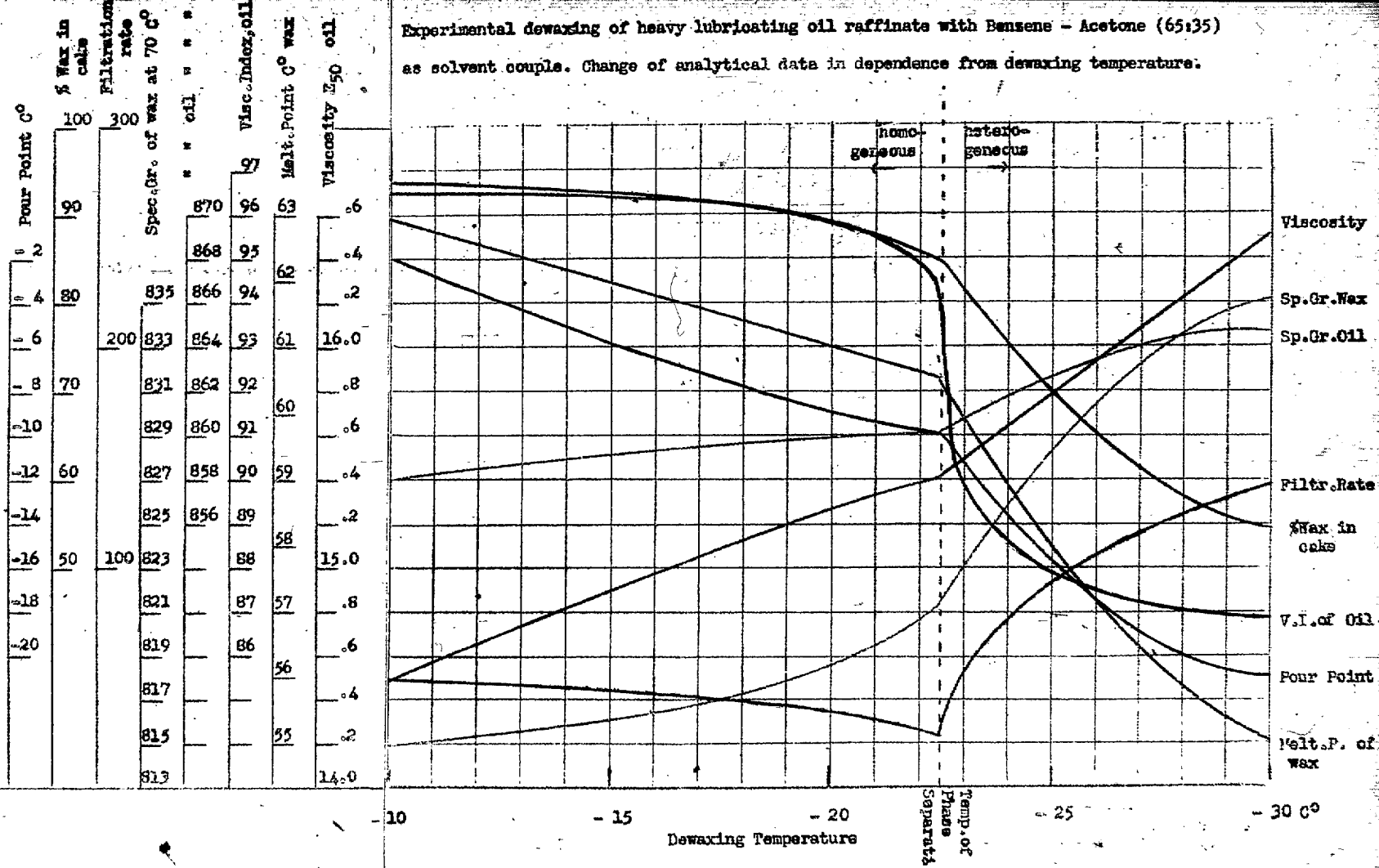
a) Filtration rate decreases. The drop in filtration velocity is only small if suitable solvents are chosen.

b) The wax cake contains oil which may run up to a few percent near phase separation. It also can be kept very low by selecting the proper solvents.

The last two results are obviously surprising because there seems to be no plausible reason for decrease of filtration rate and contamination of wax by oil

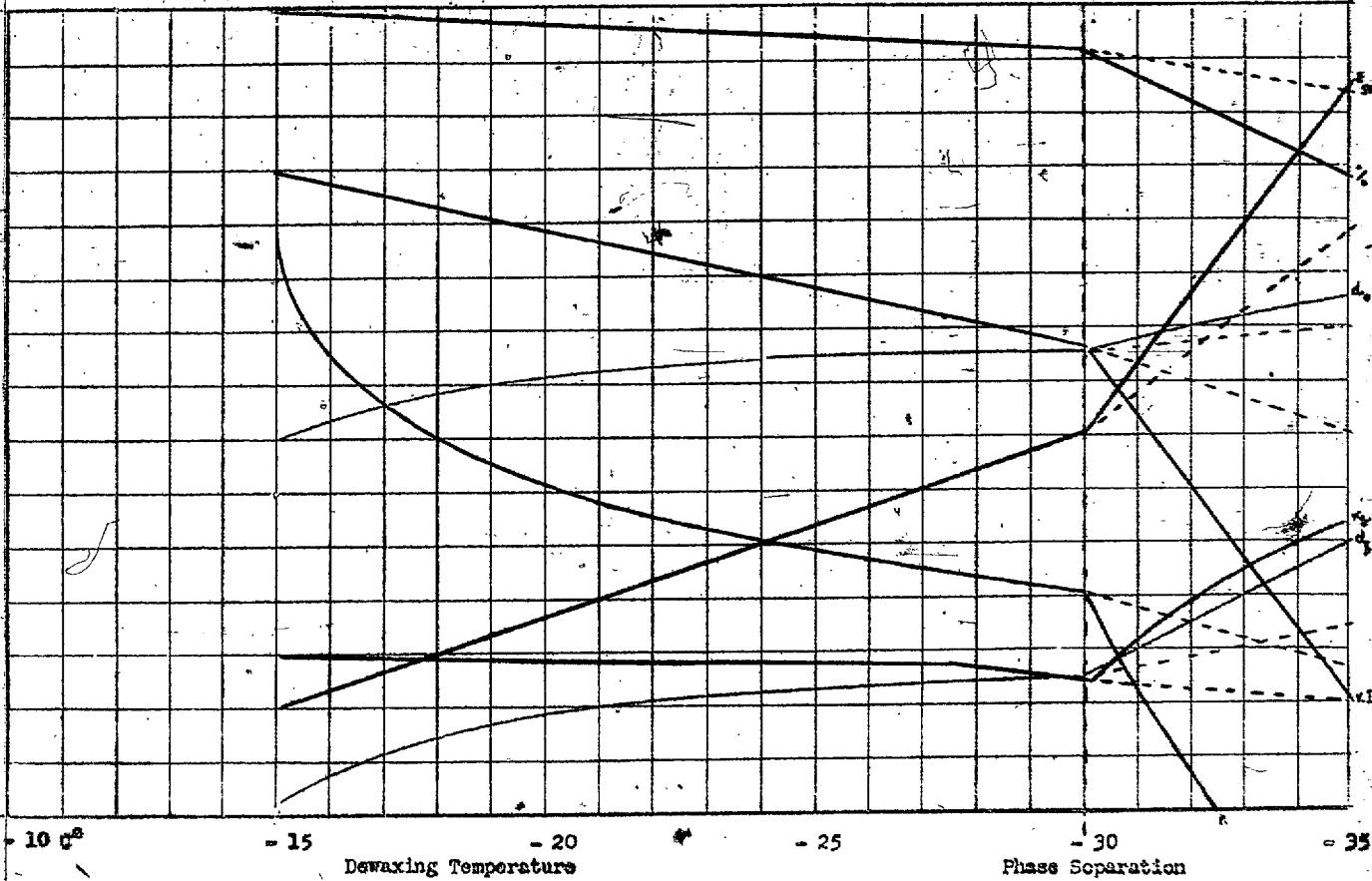
Experimental dewaxing of heavy lubricating oil raffinate with Bensene - Acetone (65:35)

as solvent couple. Change of analytical data in dependence from dewaxing temperature.



Experimental dewaxing of heavy lubricating oil raffinate with dichloromethane as solvent. Change of analytical data in dependence from dewaxing temperature. Dotted curves after shifting temperature of phase separation by addition of 10% benzene to the dichloromethane. Dilution 250%, wash liquid 250%.

Free Point °C	% Wax in cells	Filteration rate	Spec. Gr. of wax at 70 °C	Oil	Visc. index, oil	Melt. Point °C wax	Viscosity 250 oil
100							
90					870	96	8.0
					868	95	7.5
80					835	94	6.5
6	200				833	93	16.0
					854	93	6.5
3	70				841	92	6.5
10					829	92	6.5
12	60				827	90	5.5
14					825	89	5.5
16	50	100			823	89	15.0
18					821	87	6.5
20					819	86	6.5
					817	86	6.5
					815	85	6.5
					813	85	14.0



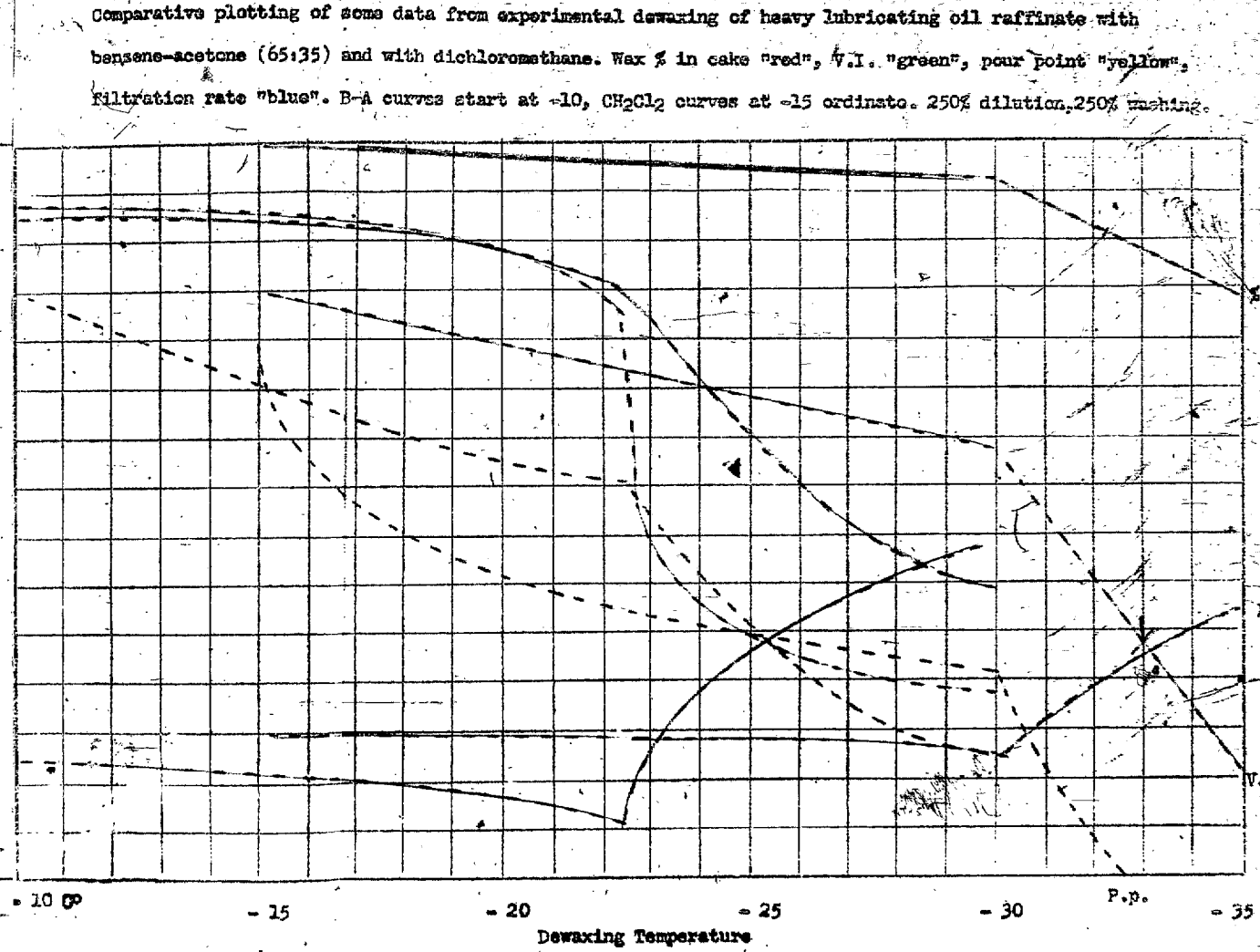
in the homogeneous field. Supported by a few simple experiments, on which no figures are available I explain the facts by adsorption of oil to the wax crystals, which increases at an extraordinary rate with decreasing temperature. Adsorption depends on total crystal surface. The percentage of adsorbed oil is therefore negligible for lighter oils with larger crystals and small total surface, while it may become amazingly high for high molecular amorphous distillates and raffinates in which the numerous micro - crystals create almost ideal conditions for adsorption. Adsorption depends also on the physical characteristics of the solvent such as surface tension. Oil adsorption to wax crystals can therefore be held back by the use of suitable diluents. Again it is some chlorinated solvents such as dichloromethane, which depress oil adsorption to a minimum as it is evident from the curves. The effect of adsorption is absolutely comparable in its consequences to phase separation, because the highly paraffinic components are preferably adsorbed and, as we have seen above, it is almost impossible to wash paraffinic oil from wax crystals for phase rule reasons. There also is prevention better than cure and holding oil adsorption low by the use of suitable solvents is the best answer to the problem. The only possible cure, however, is to give the filter cake a final wash with warm solvent, which counteracts adsorption, and to recycle that filtrate to predilution.

The decreasing filtration rate can be explained as a consequence of oil adsorption. It is not the actual filtration velocity which decreases, but the time for washing of the filter cake must be extended. Evidently an oil holding cake will be less porous and that shows in the time which is consumed for washing. The assumption is supported by the fact that chlorinated solvents which inhibited adsorption of oil show only negligible decrease of filtration rate

The dewaxing process should therefore be governed by the considerations under 1) and 2).

The most important figures which were obtained with benzol - acetone and dichloromethane were plotted on page 90 for a comparative study. The superiority

Pour Point °C	% Wax in cake	Filtration rate	Spec. Gr. of wax at 70 °C	Oil	Visc. Index, oil	Melt. Point °C wax	Viscosity %50 oil
100					97		
98					96		
96					95		
94					94		
92					93		
90					92		
88					91		
86					90		
84					89		
82					88		
80					87		
78					86		
76					85		
74					84		
72					83		
70					82		
68					81		
66					80		
64					79		
62					78		
60					77		
58					76		
56					75		
54					74		
52					73		
50					72		
48					71		
46					70		
44					69		
42					68		
40					67		
38					66		
36					65		
34					64		
32					63		
30					62		
28					61		
26					60		
24					59		
22					58		
20					57		
18					56		
16					55		
14					54		
12					53		
10					52		
8					51		
6					50		
4					49		
2					48		
0					47		



of dichloromethane is evident in all figures.

- 1) Filtration rates are higher
- 2) Lower pour points are met with less refrigerating effort.
- 3) The slightly lower V.I. of the dewaxed oil is a natural consequence of better dewaxing and unavoidable
- 4) The oil content of the wax cake is negligible.

It can be objected that similar results may be anticipated if blending proportion of benzene - acetone is suitably adjusted such as to shift phase separation to lower temperature. That is wrong because it would mean higher benzene content of the solvent which also increases solubility of paraffin and leads to rise of pour point which can only be counteracted by higher refrigerating effort. Filtration rate will be only little affected. Adsorption of oil to paraffin will be decreased indeed but the overall valuation does not indicate any fundamental favourable change.

This does not mean that benzol - acetone is an unsuitable dewaxing solvent. It is known that this solvent couple works satisfactorily in largest scale and that its flexibility is remarkable. However, the discussed chlorinated solvents are superior in flexibility and results and high quality products can be obtained with less dewaxing effort which naturally means better economy.

The example of heavy paraffinic lub oil raffinate was purposely chosen to demonstrate that liquids, which from phase rule and other considerations are perfectly suitable as dewaxing solvents show gradual differences which become most important when highest efficiency and quality demands are to be met. Such gradual differences show not so well for lighter oils, which can be successfully dewaxed with any solvent couple that meets the fundamental demands. Heavy oil, as it was shown brings up new additional view points such as adsorption and more problems are met if still heavier molecules lead over to the field of deasphaltizing which has so many view points in common with dewaxing.