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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 I

## P R E F A C E

In the following VII Articles the writer makes an attempt to summarize some results, which he obtained as head of the Edeleanu Company's research staff.

The articles are:

- I Introduction
- II Chemical Conclusions
- III Crystallographic Conclusions
- IV Filters and Phase Problems
- V Static Charge, Filter Cloth, Laboratory Research
- VI Technical View Points, Other Dewaxing Ideas,  
Miscellaneous
- VII New Electro-optical Analysis for Paraffin

I have to apologize for being unable to give exhaustive tables, graphs, and pictures, but practically all files have been destroyed as a consequence of air raids and most facts were given from memory and a few scattered notes. Several ideas are new, however, and also unknown to my company. It is hoped that they help the American oil industry a little in further advancing problems.

# A R T I C L E I

## I N T R O D U C T I O N

The problem of dewaxing mineral oil cuts or brown coal tar fractions is usually answered by the separation of the paraffinic components by means of filters or centrifuges. The oil is diluted with solvents and the mixture is chilled before dewaxing in order to have the paraffin in solid form and able to be separated from the liquid phase. This way shall be discussed in the following pages. Filtration and centrifuging are common practice in chemical industry, but many additional facts must be considered in the dewaxing of oils and the laws which govern that process must be strictly observed to dewax successfully and with optimum results.

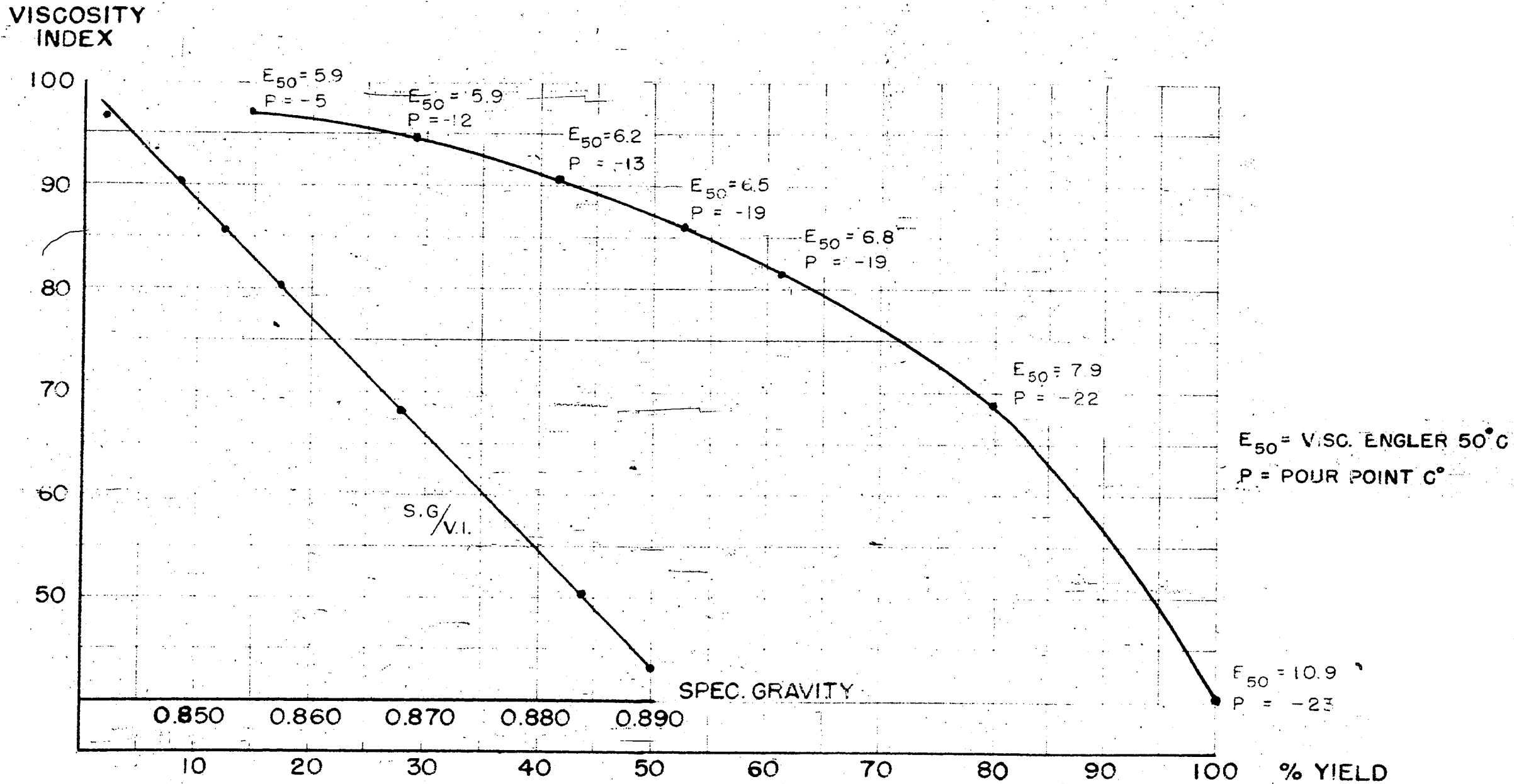
The difficulty of the process becomes evident when one realizes that it is not easy to define the final products of dewaxing, which are complicated mixtures and no chemical individuals. That involves, that their physical properties vary. They are called dewaxed low pouring oil and paraffin wax. Their characterization is as follows:

Paraffin. A mixture of saturated hydrocarbons which blend in any proportion with each other and are solid at low temperature. Any such hydrocarbon which freezes out of its solution in oil above  $-20^{\circ}\text{C}$  is to be considered as paraffin wax. It is the waxes melting above  $25^{\circ}\text{C}$  which are widely used commercially. Chemically they can be defined as saturated straight chain, branched and cyclic hydrocarbons, which may also contain small amounts of oxygen or nitrogen compounds and which are solid at room temperature. The percentage in which paraffin is present and the proportions in which the various individual components occur, depend largely on the origin of the oil.

and is different for mineral oils and tar products. They also depend largely on the boiling range of the fraction and on its pretreatment. This is why solubility and crystallographic behaviour of various waxes is so much dissimilar, which becomes evident in the difficulty to separate them and in the physical and chemical properties of the different wax cakes.

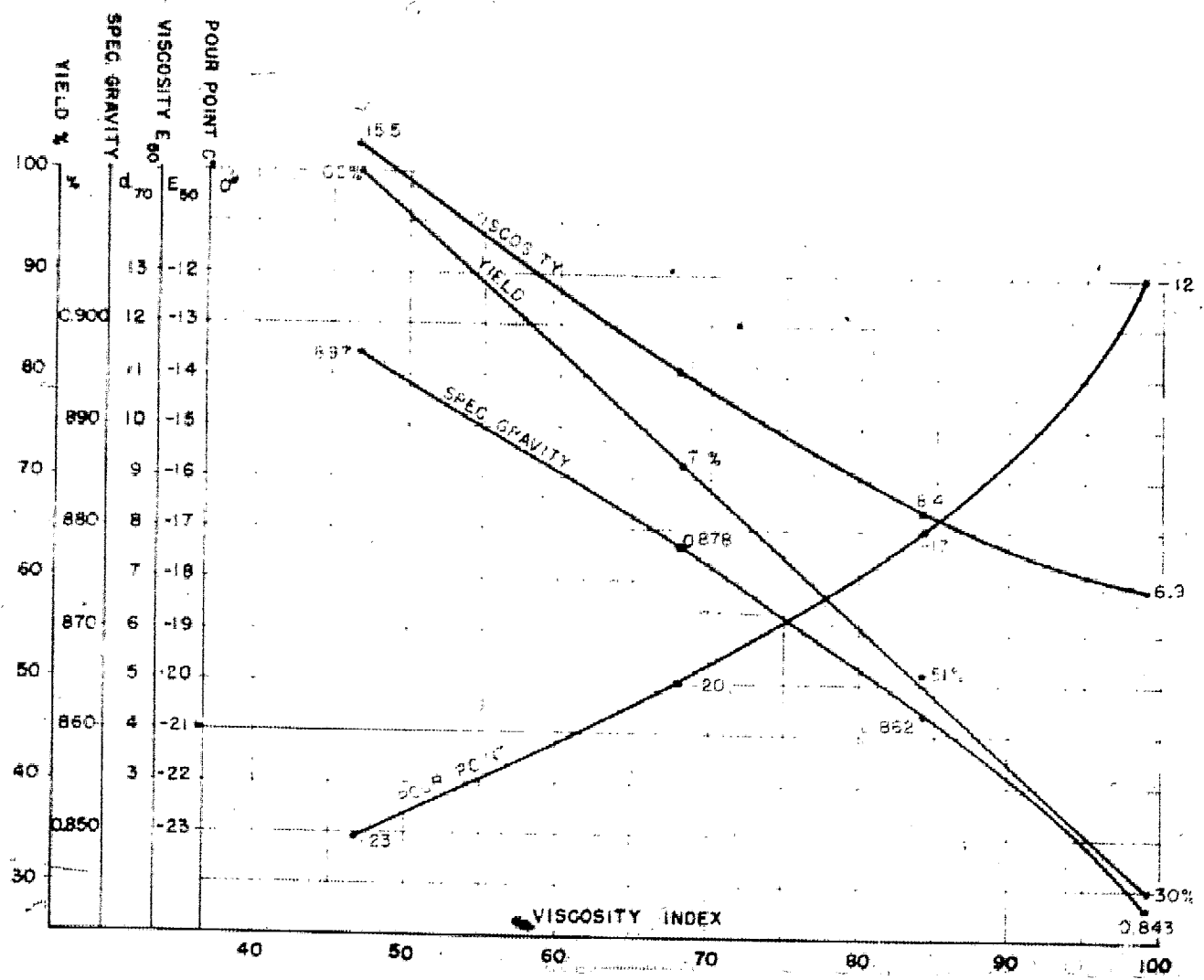
Oil. Dewaxed oil we call the oily liquid which remains after separation of the wax at low temperature. It consists of a complicated mixture of hydrocarbons and but little is known about its chemical individuals. Empirical analytical methods determine its lubricating efficiency or other characteristics which are important for its use. In connection with dewaxing it is cloud point, solid point and pour point only which interests, because it is an expression for the freedom from paraffin wax. A pour point  $-20^{\circ}$  C indicates that the oil has been dewaxed satisfactorily for most purposes, although there is no limit theoretically to lower the pour point by separating at lower temperature and eliminating compounds which solidify below  $-20^{\circ}$  C. There are practical reasons which prohibit to lower the pour point unnecessarily, however. The low melting saturated hydrocarbons have considerable chemical stability. In light cuts they have high cetane number which makes them suitable Diesel fuels, while flat viscosity curves in heavy fractions makes them high class lubricants. Their separation means a loss of quantity and quality for the oil and for the wax cake they would be a contaminant. It is to be considered, however, that refining or solvent extraction after dewaxing raises the pour point and that is why refining should be done before dewaxing. Table 3a and 3b give graphs which indicate the change in physical properties which happen to a dewaxed oil when it is submitted to progressive solvent refining. The pour point rises slowly for moderate solvent extraction but in

# CHANGE OF PROPERTIES IN PROGRESSIVE SOLVENT EXTRACTION



DEWAXED DISTILLATE FROM AUSTRIAN CRUDE, BENZENE-SO<sub>2</sub> AS REFINING AGENT.

# CHANGE OF PROPERTIES IN PROGRESSIVE SOLVENT EXTRACTION ON AUSTRIAN DEWAXED LUB-OIL DISTILLATE, PHENOL AS SOLVENT



~~production of high viscosity index oils by exhaustive solvent treatment it~~  
climbs up rapidly and beyond permissible limits. That effect can be counter-  
balanced by the addition of suitable pour point depressors, but there is also  
an economic reason for that sequence of operations, because dewaxing costs  
are higher in general, than the costs of refining or of treatment with  
selective solvents. Dewaxing of the considerably smaller quantity of refined  
stock means a substantial saving in treating costs. In exceptional cases,  
when dewaxing as the first step appears to be advantageous, it is essential to  
consider that elevation of pour points.

All this shows the difficulty to define the technical product "wax free  
oil" because a low pouring oil need not be actually wax free. It is easier  
to give a plain definition of "oil free paraffine wax" from a commercial  
point of view, thereby meaning a mixture of solid hydrocarbons which is  
perfectly free from liquid components at a specified temperature.

Analytical procedures. The difficulty to define the terms "paraffin"  
and "dewaxed oil" becomes very evident in the analytical methods. The  
classical method of Holde to separate oil from paraffin at  $-20\text{ C}^{\circ}$  in  
dilution with ether-alcohol mixtures and to weigh back the well washed wax  
scales, was pretty soon considered to be unsatisfactory. Other authors  
replaced the ether-alcohol by other solvents such as chlorinated hydrocarbons,  
pyridine, butanone, etc., and suggested other quantities for wax, dilution,  
wash liquid and temperature of filtration without making a fundamental change  
of the procedure, or getting more reliable results. Those methods were  
inaccurate because they did not consider the varying and complex nature of  
different paraffins and the solubility of wax in the comparatively enormous  
quantity of diluting liquid. It was therefore an improvement when

scientists worked out a method which was based upon weighing back the oil instead of the paraffin and on observing its pour point. Figures which were obtained by that way were closer to the results which were actually observed in running plants and still more correct data could be obtained by dewaxing of several hundred grams of input in an experimental unit with close approach to the operating conditions of pilot plants or industrial factories. The author suggested a basically new analytical procedure which eliminates dilution entirely and measures the content of solid paraffin hydrocarbons at any specified temperature by determination of double refractivity and turbidity in a quick and simple way. (See annex) This method fails at very low wax contents, but the analyses which are based on precipitation do not give reliable results in this case either. It can be anticipated that the optical method is more likely to be developed for that special purpose than a procedure which works on the principle of dilution with solvents and refrigeration. Other physical ways of testing measure the anilin point, the refractive index, the hardness by penetration of balls or pins and the tenacity, or they simply force out surplus oil under high pressure. These tests are not based on specific properties of wax or oil and are only empirical means to compare the change of the general quality of a highly waxy commercial product. They can, therefore, hardly be used for examination of any grade of wax, wax slops or waxy oil.

The analytical methods to test the dewaxed oils for absence of paraffin were not given basic or even considerable changes. Cloud point and pour point are the expression of a technical quality and that is all that is asked from the dewaxing point of view. The refiner wants to know how paraffinic his final product will be and he has special tests for that purpose. For the



dewaxing expert it is all the same, however, whether his pour point is fixed by a certain content of soft paraffins or by traces of hard wax or by viscosity as long as it is low enough. Therefore, changes in analytic procedure extended to an alteration of chilling rate, temperature gap, discovery of turbidity in strongly colored oils by infrared light and photo-electric cell rather than in development of fundamentally new procedures and that is why all those tests did not give much chemical information either.

Technical processes. The original dewaxing process was simple chilling of the waxy oil to moderately low temperature and filtering it through cloth under static pressure. Cold settling followed. It became soon obsolete. Filter presses, refrigerating outfit and chillers of various design were developed and the oils were prediluted with mineral oil cuts. The poor quality of wax and oil made further research imperative and further improvement was obtained by tricks in distillation, by the use of filter aids such as diatomaceous earth and by subdividing the filtration in stages. Sweating was one of the first processes to improve further the quality of the slack wax. - It was soon found that centrifuges were the answer to separate successfully the so-called amorphous paraffins, occurring in the higher fractions and which could not be economically separated by filtration. Low and high speed centrifuges were adapted to that special problem. Dilution with gasoline was discarded because it was not only dangerous, but made a huge gap necessary between dewaxing temperature and wanted pour point, due to the comparatively high solubility of paraffin in gasoline even at low temperature. Dilution with other solvents, alien to the oil, gave better calorific data and exhibited less solubility for wax, and the introduction of chlorinated hydrocarbons of high gravity offered advantages in centrifuge design and operation. There was doubtlessly large progress in

~~improving wax and oil quality at the same time, decreasing processing costs.~~  
It remains doubtful if the use of propane for dewaxing was not a step backward because it increased again the gap between dewaxing temperature and pour point although solubility of wax in propane is lower than in gasoline cuts and it was also highly inflammable. It was an effort, however, to combine two processes which depended on one solvent only. A better answer was given by the combination of Benzol-SO<sub>2</sub> for extraction and for dewaxing afterwards with the same solvents blended in reverse proportion. This solvent combination gave good results which compared favourably with the Benzol-acetone dewaxing process which was discovered about the same time and turned out satisfactory oils, the wax cakes still requiring further improvement. Numerous patents indicate the result of extensive laboratory research which covers the field of dewaxing by such means as repulping, recrystallization, recycling of wash liquid to charging stock, addition of the solvent in stages with chilling in between, etc. Although these improvements were advantageous with regard to quality and decrease of treating costs, it was generally little known why speed of filtration increased and why the final wax had a better quality.

Recent research found the answers and examination of dewaxing problems from the view point of the phase rule and crystallographic behaviour of paraffin crystals led to a general consideration of the dewaxing problem as a whole.

It is obvious that the possibilities to further improve the dewaxing process are by far not exhausted but the ways have been disclosed.

The knowledge about the fundamental rules which are governing dewaxing permitted considerable progress which culminates presently in the design of special filters (band filters working on the principle of a continuous

Buchner funnel developed and designed by the EDELEANU-Co.) the use of new solvent combinations which are adapted to the job by strict consideration of phase rule laws (dichloro-methane and dichloro-ethane) and by subdividing the dewaxing into steps which allows the production of various kinds of oil free waxes which the market is asking for. The quality of the dewaxed oils has hardly been touched by the recent development, naturally so, because low pour points could be obtained according to specifications with older processes also. But now the pour points can be met with less effort which means lowered treating costs. Wax and oil can both be made now to answer the request for top quality and any desired pour point of the oil and any melting point for the oil free paraffin may be obtained.

The wide field of activity which is still open for the chemist and the engineer is chiefly with regard to treating costs and simplification of the separating apparatus. Other solvents may be discovered which require less dilution or which are more economic as far as heating and cooling problems are concerned. The design of the chillers may be changed fundamentally. They are very unsatisfactory from the theoretical point of view as it will be seen below. It is the chillers in fact, which are the most expensive bottle neck of the dewaxing units and they are the trouble spot as well, which may cause an awful mess in the plants in spite of all careful theoretical considerations. Filtration and evaporation are likely to cause trouble chiefly if the chillers fail to work properly due to poor design or if phase equilibrium is disturbed by them. Little problems only exist in filtration, if the feed stock to the filters meets specifications.

Finally there always remains the possibility, that an entirely new process is invented which does away with filtration and makes all known processes obsolete.