

42

ADVANCES IN SOLVENT-  
DEWAXING OF MINERAL OILS AND TARBS

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A R T I C L E I

CHEMICAL CONCLUSIONS

## ARTICLE II

### CHEMICAL CONCLUSIONS

The study of the most suitable dewaxing conditions presumes the knowledge of the crystallographic behaviour of paraffin waxes which depends on molecular weight and chemical constitution. Waxes may be composed of just a few different types of saturated hydrocarbons, that is straight chain, branched and cyclic with more or less branched side chains. The straight chain homologues are limited in number and well defined, whereas the number of isomeric paraffins and of branched hydroaromatic compounds runs theoretically into millions. It is unlikely that all those possible compounds occur in natural products because oils, tars and bitumen have been generated by decomposition of organic matter, representing a limited number of compounds. Its conversion to petroleum products breaks down the molecules to less complicated structures. Basic matter and conditions of conversion determine the extent of that reaction and the type of paraffin formed. It seems therefore feasible to assume that comparatively few compounds are generated and predominate in waxes which also indicate their origin. This is confirmed by the fact, that synthetic waxes from hydrogenation of carbon monoxide as a simple well defined carbon source give preferably well defined straight chain homologues. Brown coal tar is derived from more complicated basic material, fundamentally of vegetable character. Its paraffin is low molecular and highly isomeric non cyclic. It is easily broken down by heat to straight chain paraffins. Mineral oil, in contrast to tar extends over a wide

range of molecular weight. That is what it has in common with synthetic products, but it is derived from complicated compounds of animal origin and therefore also contains cyclic derivatives. Still the consideration will hold true, that the number of its constituents is limited. Separating a paraffin into its component groups of different structure and splitting the groups into a few fractions of different molecular weight and physical characteristics will permit a rough classification of any paraffin wax and give information about chemical type and crystallographic peculiarities, even though no well defined chemical compounds were obtained. The molecular weights under consideration range from 250 - 1500. Separation of waxes by distillation and crystallization from solvents have been frequently described in literature. It is the chosen solvent and the larger number of crystal fractions which were different in our procedure. Distillation is to be discarded with regard to the instability of low molecular branched waxes to heat, but all efforts to replace it by a solvent extraction in separating to molecular weight, failed. Distillation was therefore done in good vacuum and without fractionation, collecting only 4 - 5 cuts and a residue and leaving the further splitting to molecular weight to the fractional crystallization with solvent. Separation to different chemical structure was effected with the solvents which the Eddeleanu process uses extensively in commercial plants, that is dichloromethane and dichloroethane, two of the highest selective solvents to molecular structure. The wax cut was dissolved in 500% solvent at elevated temperature. Blending ratio of the two solvents was adjusted to meet phase rule requirements which are discussed further below. Chilling was done at a rate of 1 C° in 3 - 5 minutes and the stock was filtered

through a Buchner funnel when separation of wax became visible. Ample wash liquid was used regardless of the solubility of wax in solvent, which was recovered by evaporation of most of the solvent in vacuo and recycled to the charging stock. The next fractionation was done 2 C° lower than the previous one and so forth until 20 - 40 fractions had been obtained. The yield of some fractions was negligible, while others were abundant. The job is time consuming but for 5 cuts and the still bottoms it furnishes more than 100 fractions of wax, which may partly consist of chemical individuals but in their majority at least break down the complicated initial mixture of paraffinic hydrocarbons into groups which consist of but few components. For general information there seems to be no need for such a detailed separation and larger steps in crystallization are permissible. The fractions are then more complex, but the saving in time is considerable, and general conclusions about chemical character and crystal properties can also be drawn.

Prof. Dr. E. Terres, in a speech addressed to the German brown coal syndicate, suggested to plot molecular weight of such fractions against melting point and to compare the graph with the corresponding curve of straight chain paraffins. (13) This gives a general survey indeed and shows how far in average a wax is different from straight chain character. But melting point alone is no sufficient characteristic, especially of obviously impure chemicals, and no conclusions can be drawn with certainty. Also the indication of curves of coordinated hydrocarbons from such a graph must appear doubtful. The chief handicap lies in the fact that branched and cyclic paraffins have both lower melting points than equimolecular straight chain waxes and therefore cannot be discerned. Three facts can be derived with certainty from those experiments, however, that is 1) Separation of wax

in small even steps does not give a series of preparations with nearly the same yield and continuous slope of melting point, but furnishes fractions which are very different in yield, and show gaps in fractional crystallization in which practically no wax is separated. 2) Melting point plotted against yield of fractions gives no continuous curve but indicates steps. (14) Both facts point to the existence of only a limited number of individual paraffinic hydrocarbons in paraffin wax, but say nothing about constitution. 3) Up to average molecular weight of approximately 400 the existence of straight chain compounds in all paraffin waxes is predominant, Isoparaffins occur abundantly in tars but are mostly broken down in distillation to less or unbranched waxes. With increasing molecular weight the unbranched paraffins become scarcer in natural products and seem to be absent for molecular weight above 1000. It will be seen later that those wax components are partly isomeric partly cyclic between 400 and 600, while they are doubtlessly chiefly cyclic above 800.

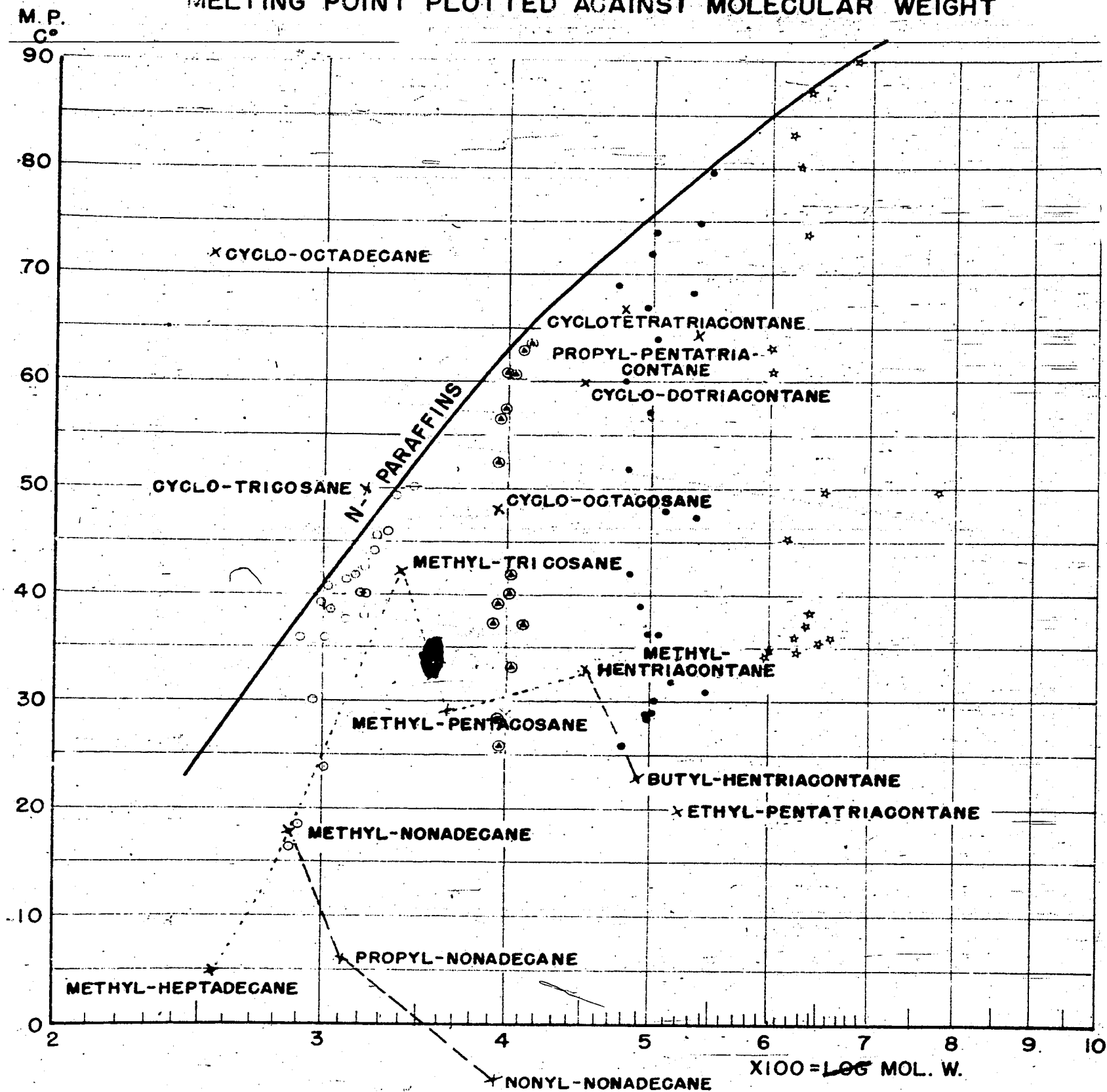
In 1942 an article was published by Gross and Grodde (Deutsche Erdoel A.G. mother company of the Edeleanu Co.) (Oel und Kohle 38, 419) in which an attempt was made to characterize a paraffin wax by 2 numbers, which were called the "Asymmetry value" and the "Ring value", the first to give an indication of branched side chains, the second to reflect the extent of cyclization. Both figures were based on further development of the formulas of Etessam and Sawyer and of Ivanowsky. These two figures:

$$AV = 311 \cdot \frac{M}{M - 95} - 205 - 0,75 \cdot \text{Melt. Point}$$

and

$$RV = 10^3 \cdot d_{900} - 511 - 311 \cdot \frac{M}{M - 95}$$

# MELTING POINT PLOTTED AGAINST MOLECULAR WEIGHT

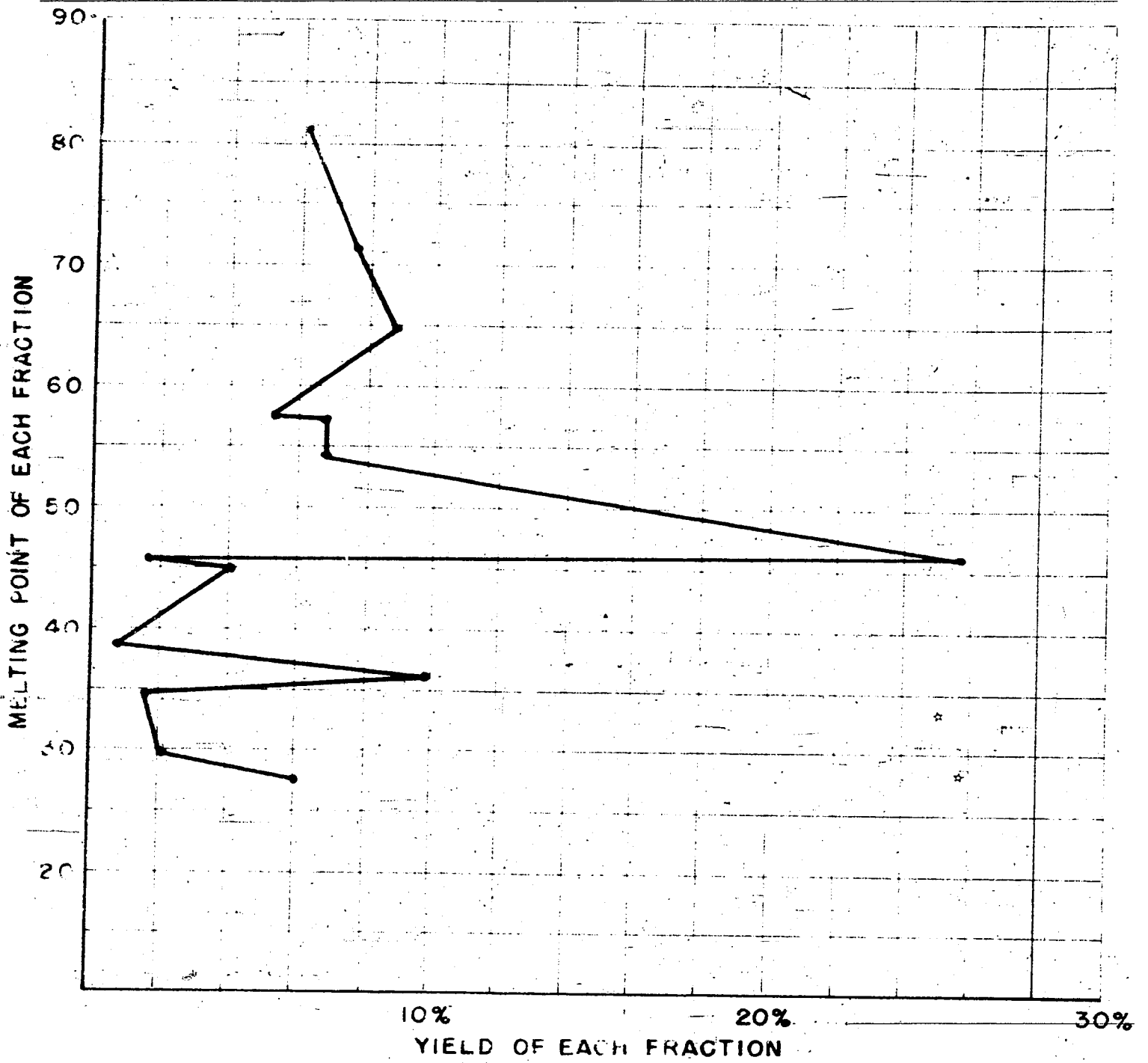


MELTING POINTS OF  
WAX FRACTIONS FROM AUSTRIAN CRUDE

- LUB CUT I
- LUB CUT II
- ★ LUB CUT III
- SPINDLE OIL CUT
- x KNOWN HYDROCARBONS

DATA FOR ISOPARAFFINS AND CYCLANES  
FROM: EGLOFF, PHYSICAL CONSTANTS  
OF HYDROCARBONS  
AND: GRUSE AND STEVENS, CHEMICAL  
TECHNOLOGY OF P.

MELTING POINT / YIELD IN FRACTIONATION OF PARAFFIN WAX  
FROM A SHORT LUBRICATING OIL CUT



<u>°C</u>	<u>%</u>
81	6.2
71	7.8
64.5	8.9
57.5	5.3
51	6.9
54	6.9
46	25.6
45.5	1.7
45	4
38.5	0.7
30	9.8
34.8	1.7
29.5	2.2
27.5	6

permitted to draw conclusions to the chemical character of waxes. Commercial products were separated into individual fractions by distillation and solvent filtration with dichloroethane similar to the procedure which was used in the Edeleanu laboratory but with less effort in fractional crystallization. While those figures could be used with advantage to characterize a single product they still were not sufficient to give more exhaustive information about commercial waxes, because they could not be plotted in an easily legible graph together with molecular weight and quantity. If both figures were contracted to a sum, however, as the authors suggested, then there was no advantage over simple plotting of melting points.

It was therefore tried to link molecular weight and percentage with specific gravity and melting point in a graphic pattern, which is capable of reflecting roughly the chemical structure and crystal peculiarities. Yield percent are obtained by weighing the crystalline fractions, gravity and melting point can be easily determined with great accuracy by conventional methods but the determination of molecular weight involves some difficulties and a few words shall be said about it.

The waxes from tars and mineral oils under consideration are within the limits of 250 - 1000. Synthetic paraffins reach to 1500 and far above. Chemical individuals will be present very seldom only and the analysis will give average molecular weights of more or less complex mixtures. No known method works entirely satisfactorily for this particular task. The standard method of measuring the rise in boiling point of a suitable liquid gives very unreliable results, because too little wax can be dissolved if one is to stay within concentrations, for which the laws of diluted solutions are valid. Better results are obtained with the kryoscopic method in benzene, which works fairly well for low melting paraffins and which may be modified



with p - dichlorobenzene for average molecular waxes. It does not work so well with high molecular and high melting waxes for the above named reason, or, on the contrary, because solubility is too small to give decent melting point depression.

Fractional separation of high melting waxes may also cause erroneous results. Staudingers method to calculate molecular weight from the viscosity of diluted solutions was also tried. This method, which gives good results for higher polymerics, gave no reliable results for waxes of average molecular weight. Satisfactory and reproduceable results were only obtained by measuring the melting point depression of naphtalene, which also gave comparable results for high melting waxes. The figures also seemed to be more reliable than those which were obtained with camphor. The calculation of molecular weight from surface energy with Foetvoes's rule gave mostly doubtful results. It is a quick method however, which required measuring of capillarity and of specific gravity at two temperatures only. Capillarity is easily measured by the rise of molten wax in fine bore tubes and no difficulty is involved in determining the specific gravity correctly in a pycnometer. Molecular weight is then valuated from the formula:

$$M = \frac{k \cdot (\theta_2 - \theta_1)}{\frac{\gamma_1}{\delta_1^{2/3}} - \frac{\gamma_2}{\delta_2^{2/3}}}$$

It means k Foetvoes constant 2.12 ergs,  $\gamma$  surface tension, h rise in capillary tube, r diameter of tube in cm, g gravity 981.1 cm/sec<sup>-1</sup>,  $\delta$  spec. grav.,  $\theta$  abs. temp.

In an unpublished report I suggested to plot wax composition such as follows: Molecular weights are logarithmically plotted on the abscissa. The ordinate was to reflect chemical structure. A characteristic was chosen which varies widely with molecular constitution. It is the product obtained by multiplication of the difference of specific gravity at 90°C and of the melting point of the fraction from the corresponding data of the equimolecular straight chain paraffin. This figure may be called classification number and it ranges from 0 to 10 000 for most waxes. It is plotted logarithmically and is evidently zero for straight chain waxes only. There is no large difference in specific gravity of unbranched and isomeric paraffins, but the melting point drops substantially in branched waxes, which is therefore indicated by that number. Cyclic waxes have higher specific gravity than normal ones and simultaneously lower melting points and this is still considerably more pronounced for hydroaromatics. The number therefore grows to quite a different order of magnitude, reflecting the number of rings and, though much hazier, the character of the side chains. The product naturally turns towards the negative if the melting point is higher or the spec. gravity lower than that of the equimolecular n - paraffin.

Evidently this method cannot claim analytical accuracy. No law is known which formulates melting point depression or rise of specific gravity in dependence from isomeric structure or cyclization. Furthermore the fractions are no pure chemical individuals and their melting point will therefore be depressed anyway, even if they are close to normal paraffin character. But it has to be considered that even the attempt for a rough classification may be useful with regard to general dewaxing questions. Melting point depression for reason of impure preparations can be partly compensated by suppressing the zero point on the ordinate. It is known, that synthetic

waxes have chiefly straight chain character. If a synthetic wax is separated as described above and the result plotted in the graph this will show where the abscissa should cut the ordinate to reflect the synthetic wax fractions as straight chain compounds. This is the 30 point and all fractions with classification number below 30 shall therefore be regarded to be n - paraffins.

The spaces in which isomeric, monocyclic, and polycyclic paraffins occur are found by analysis of a larger number of fractions with Watermans ring analysis or with Gross and Groddes method. Boundary lines can be drawn which separate fields of similarly built molecules. Any unknown sample can then be separated and plotted in the graph, and check tests always showed that the location of such obtained spots reflected well the chemical structure and crystalline properties. This is not surprising if it is considered that the graphic plotting is based on physical data which are somewhat blurred indeed; but that compensation to come closer to the truth was found by correct analyses.

The classification number is little sensitive to errors of  $\pm 10\%$  in the molecular weight. It varies with molecular weight and is between 30 and approximately 1000 for iso-paraffins and cyclanes, whereas it grows from 400 to above 10 000 for hydroaromatic waxes. The boundary lines, which separate the cyclic spaces can be considered straight, but they are inclined to the abscissa. They can be shifted to run almost parallel to the abscissa by multiplying the classification number with  $\frac{\log \text{Mol. Weight}}{100}$ .

The figure reflects then the chemical character all over the range of molecular weight, but it is inferior in graphic plotting because the isoparaffinic

spots move too close together.

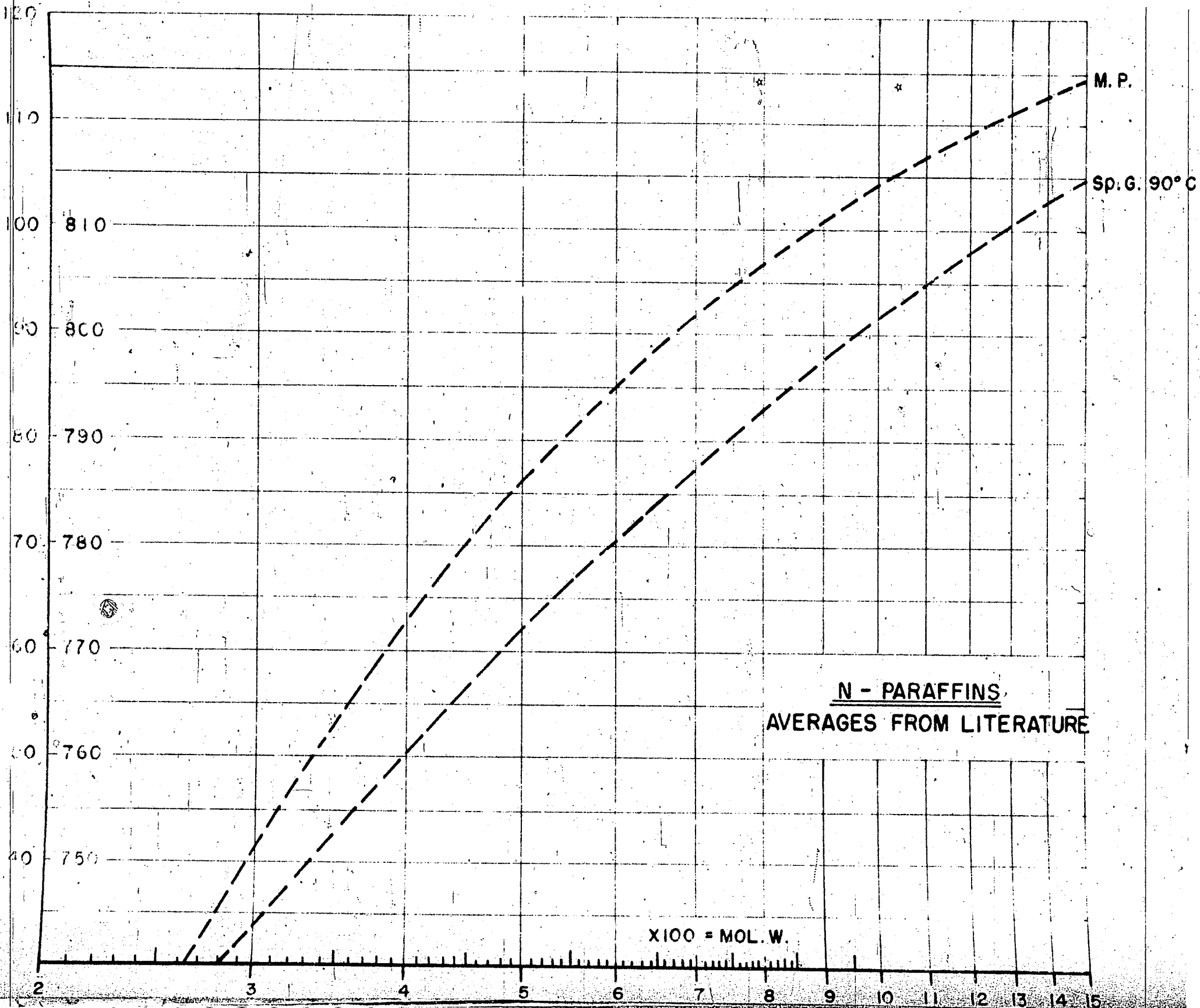
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There remains still the percentage of each obtained fraction. It is plotted on a third coordinate which extends in space but is easily readable in the graph. Arrangement of the 3 coordinates in 60° angles, together with the logarithmic plotting helps to straighten curves and facilitates survey.

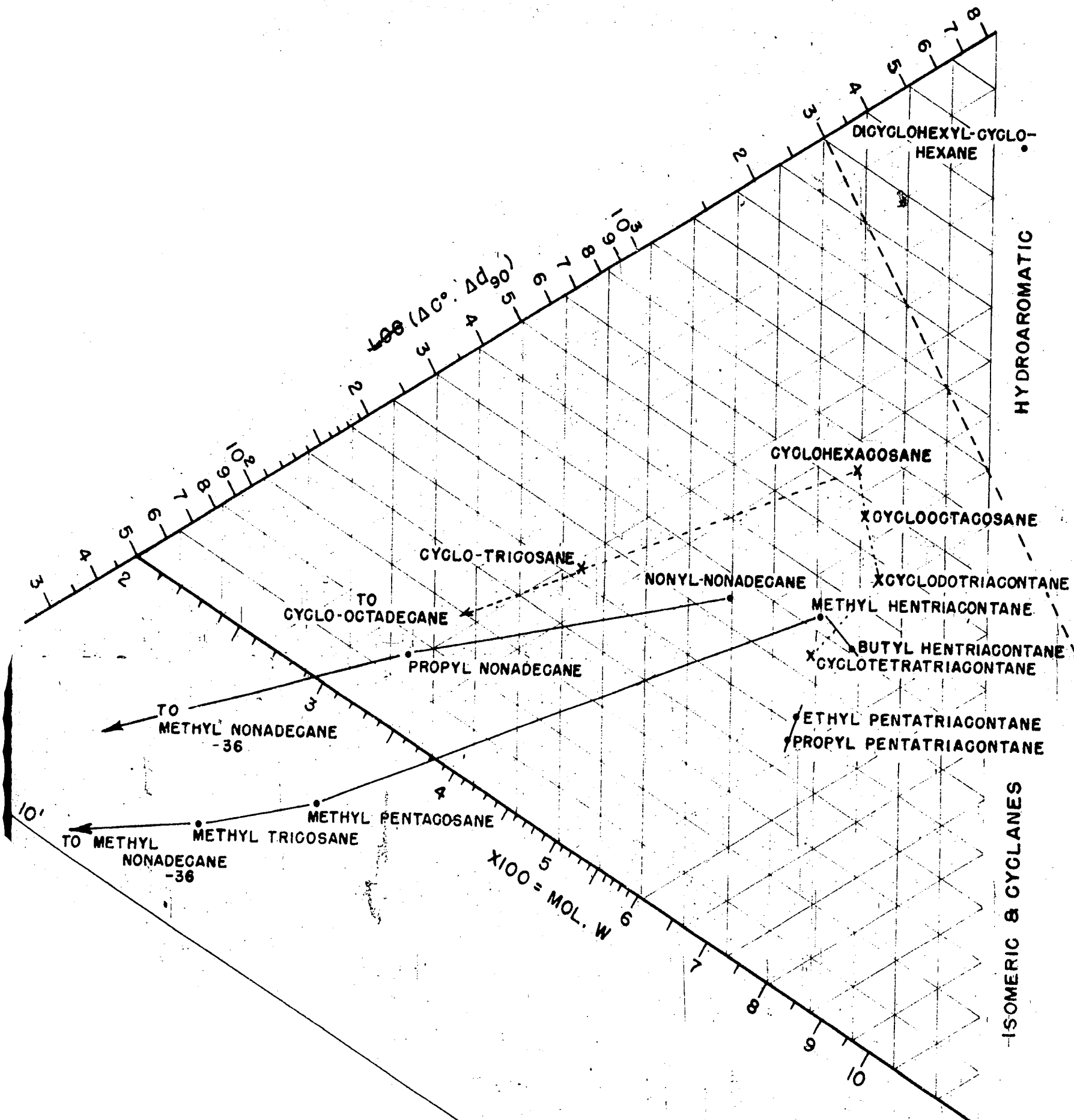
The separation of 5 paraffins is plotted on page, (22) each in a different color.

The large number of analytical data which had been obtained in our laboratory were destroyed during the war, and this method of plotting is therefore demonstrated on less exhaustive data from literature, which were taken and calculated from Gross and Groddes paper.

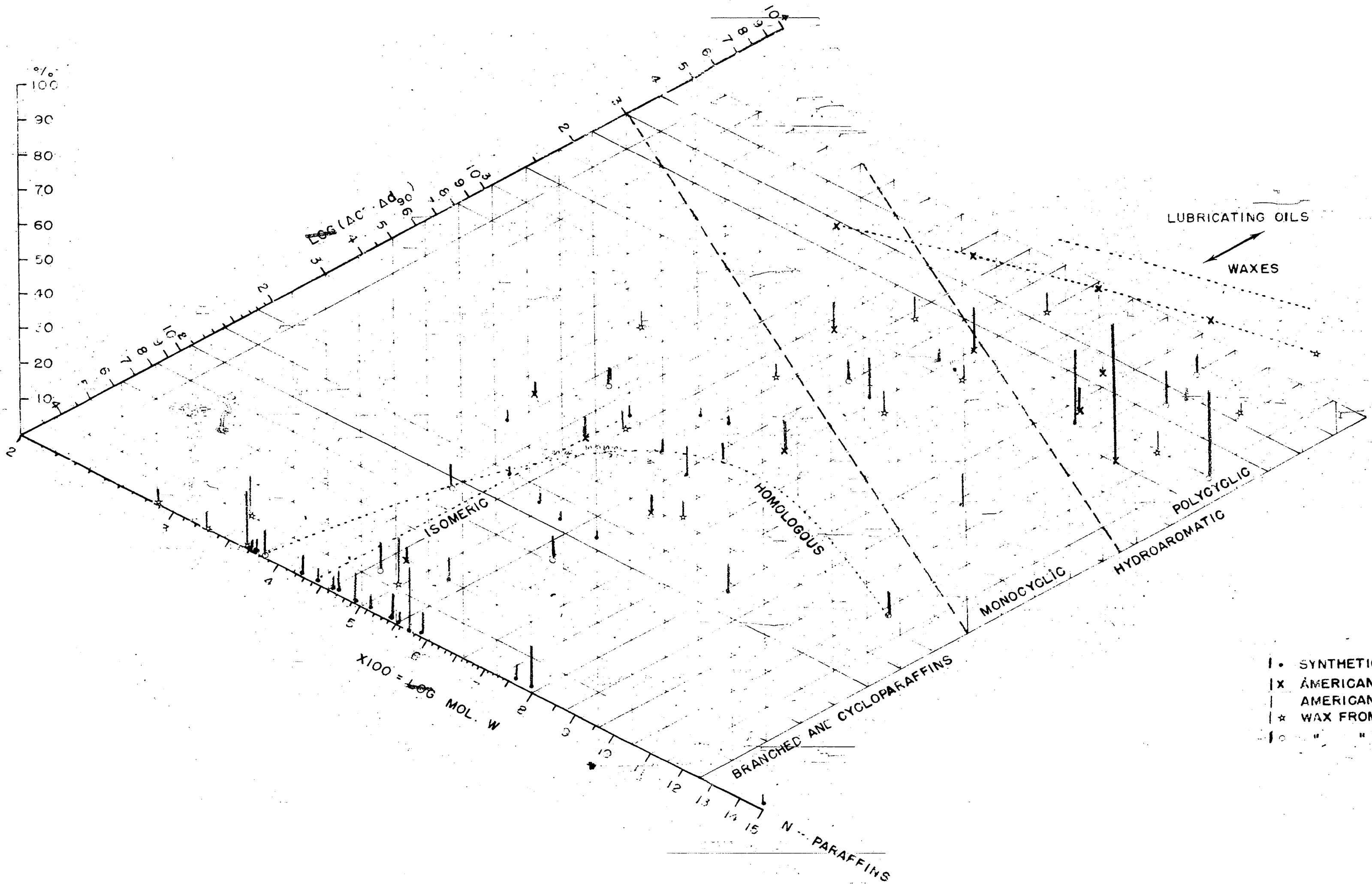
M.P. Sp.G.  
C° d<sub>90</sub>



# PLOTTING OF SOME KNOWN COMPOUNDS

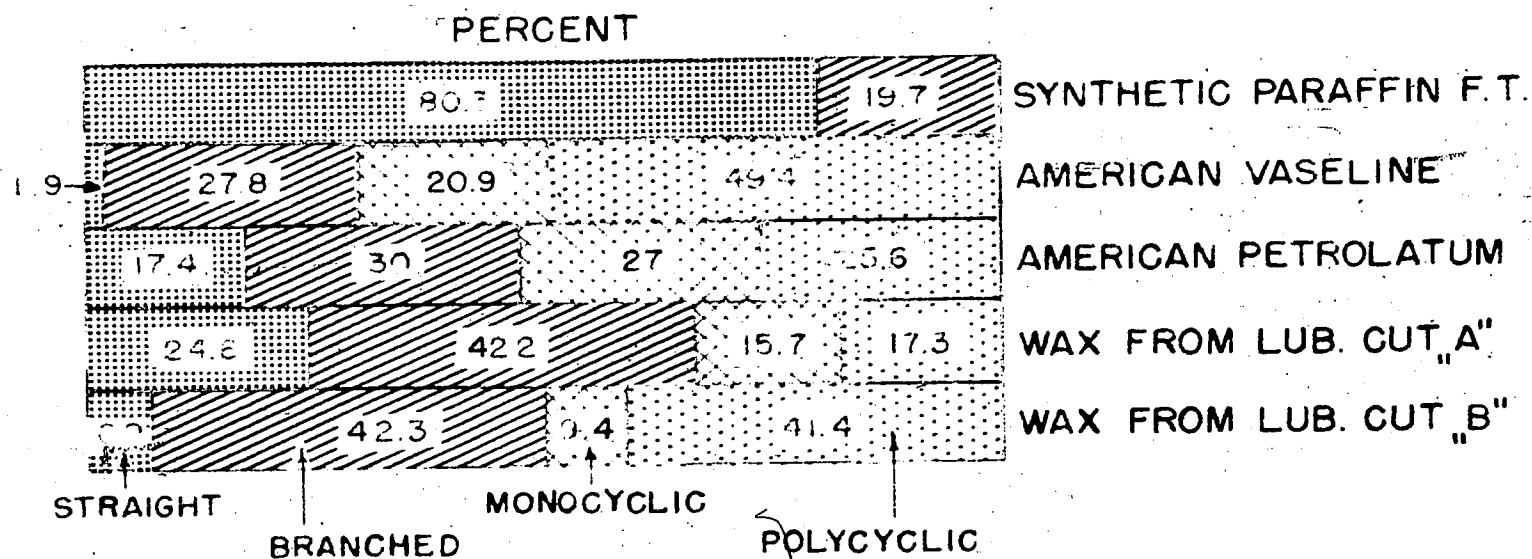


DATA FROM: GRUSE & STEVENS,  
 CHEMICAL TECHNOLOGY OF PE-  
 TROLEUM  
 AND: EGLOFF, PHYSICAL CON-  
 STANTS OF HYDROCARBONS

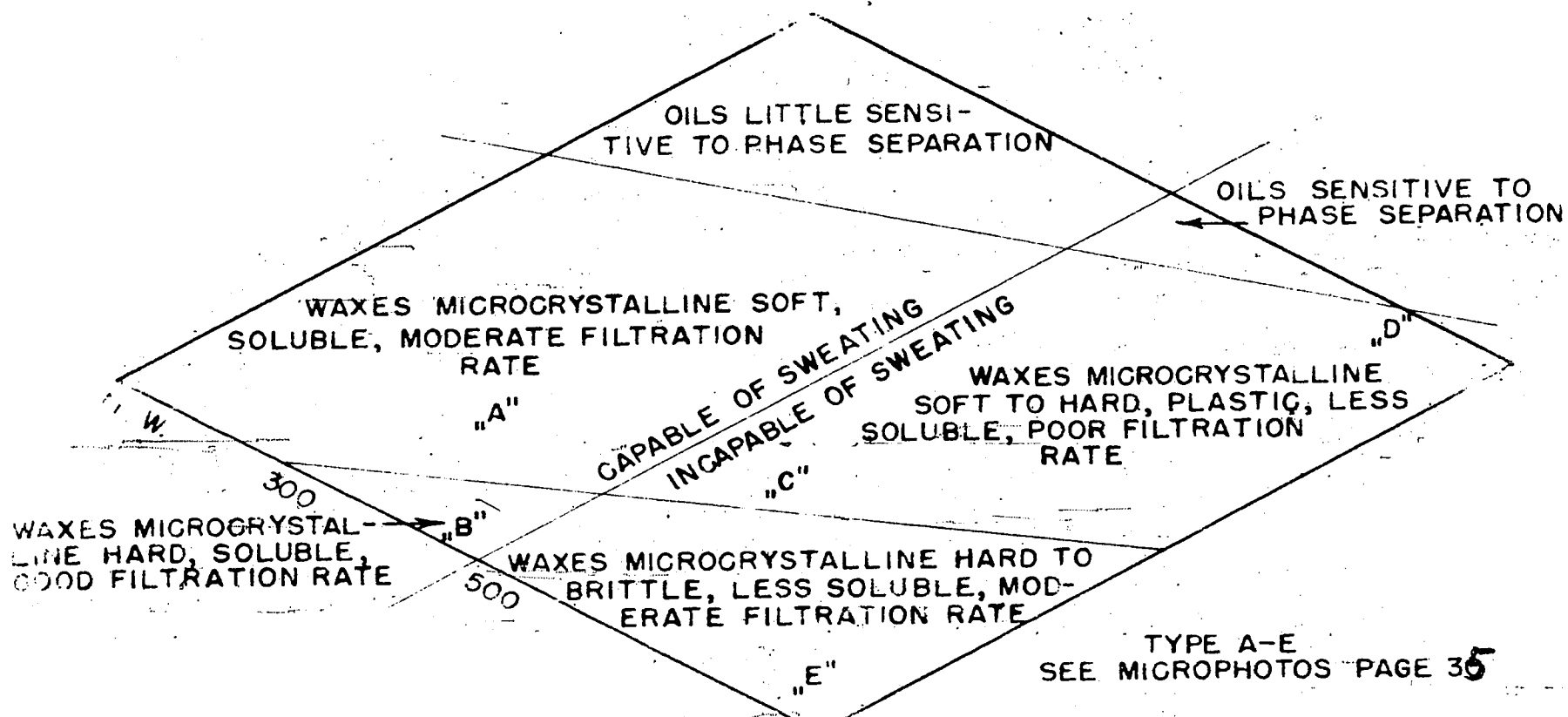


- SYNTHETIC PARAFFIN F. T.
- x AMERICAN VASELINE
- AMERICAN PETROLATUM
- \* WAX FROM LUB CUT A
- " " " " B

## CHEMICAL VALUATION OF GRAPH



## PHYSICAL VALUATION OF GRAPH





Synthetic Paraffins from Fischer - Tropsch process

(red spots)

	Yield %	Mol. W.	Melt. P.	Sp. G. 90°D	Class. No.
I	4,0	443	66,5	0,770	14
II	3,4	375	57	0,760	3
III	3,3	379	36	0,766	201
I	7,3	470	69	0,770	8
II	5,7	428	61,5	0,768	26
III	2,2	438	46	0,771	138
IV	2,9	442	24	0,772	322
I	9,3	495	71,5	0,773	9
II	4,4	467	68,5	0,771	10
III	2,6	489	43,5	0,774	126
IV	2,4	486	21,5	0,778	428
I	9,3	546	76,5	0,778	10
II	4,9	515	65,5	0,775	12
III	3,0	529	40	0,778	117
IV	1,4	521	23	0,782	448
I	7,3	591	83	0,781	2
II	3,0	556	70,5	0,779	21
III	1,9	582	44	0,782	120
I	2,1	1500	113	0,805	20
II	12,1	800	96	0,791	2
III	4,6	765	80	0,789	30

American Vaseline

(blue spots)

I	1,9	370	57	0,763	0
II	2,5	366	36,5	0,770	273
oil		360	-13	0,798	2924
I	3,9	474	67	0,776	49
II	6,2	438	54	0,781	240
III	8,0	463	25	0,797	1363
oil		464	-16	0,813	3960
I	6,2	587	68	0,791	176
II	9,0	594	52	0,794	462
III	12,9	593	21	0,810	1920
oil		606	-15	0,830	4900
I	40,3	988	111	0,825	1140
II	6,5	818	36	0,824	1860
III	2,6	770	25	0,830	2660
oil		774	-7	0,849	5814

American Petrolatum

(yellow spots)

	Yield %	Mol. W.	Melt. P.	Sp. G. 90°C	Class No.
I	6,6	524	70,5	0,780	51
II	4,2	510	53	0,784	288
oil		501	4	0,855	5976
I	17,4	571	79	0,786	32
II	9,6	562	65	0,792	255
III	13,5	595	44,5	0,802	891
IV	2,3	590	34,5	0,812	1526
oil		603	0	0,858	6545
I	8,5	807	84	0,803	130
II	11,2	899	60	0,812	574
III	21,2	843	42,5	0,825	1695
IV	4,4	942	37	0,843	2860
oil		889	2	0,886	8811

Wax from German Crude A

(green spots)

I	4,6	330	45	0,753	12
II	3,9	287	35	0,751	30
I	16,1	369	56,5	0,759	1
II	11,6	337	45,5	0,758	38
III	4,1	351	28,5	0,780	663
I	12,9	499	66	0,775	40
II	6,0	457	52,5	0,783	296
III	4,0	491	38	0,790	740
IV	5,7	512	22	0,808	1980
I	3,8	611	73	0,796	195
II	5,8	625	48,5	0,805	885
III	4,2	634	33,5	0,811	1526
IV	5,9	606	21	0,833	3380
I	6,7	1010	51	0,836	1836
II	2,4	1032	33,5	0,850	3360
II	2,3	967	16	0,878	6690

Wax from German Crude B

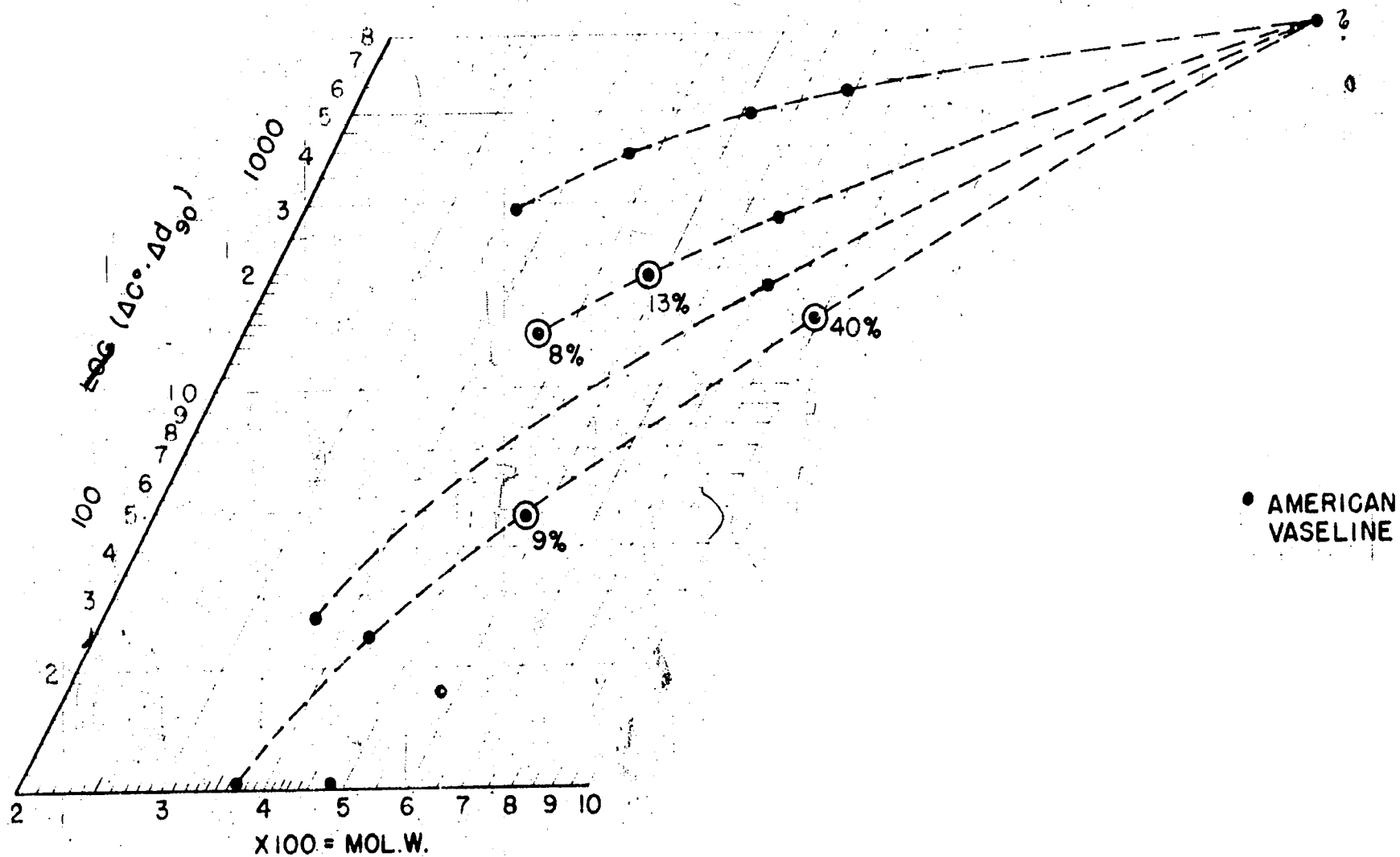
(lilac spots)

I	6,9	382	54	0,763	30
II					
I	8,0	468	64,5	0,773	42
II	6,9	414	57	0,773	99
III	4,0	397	45	0,782	374
I	7,8	577	71	0,786	84
II	5,3	566	57,5	0,792	343
III	7,2	550	39	0,799	966
I	6,2	1070	81	0,812	200
II	25,6	1185	46,5	0,836	1812
III	9,8	904	36	0,839	2665
IV	6,0	868	27,5	0,847	3697

It cannot be the result of a simple separation method to give exhaustive chemical information about the individual components of a wax, but the splitting into related groups indicates the chemical character in average. From Yield % and location of the fractions in the graph it becomes evident to what extent the wax is cyclic, branched or straight chain. Isomeric and homologous groups can be discerned. The former are located on parallels to the ordinate, while the latter ones are curves which, with increasing molecular weight cross the abscissa in sort of a parabolic slope. There is indication of but few of such homologous series, which is not surprising if the large number of possible homologous series and the rough separation into comparatively few fractions is considered. However, it is frequently possible to draw curves through points, which represent increasingly branched and cyclic compounds with growing molecular weight, finally leading to the lubricating oils. One example is plotted on page (27) for American Vaseline and it seems to indicate, that those fractions can be conceived as cleavage products of a single, or of very few complicated and high molecular compounds, which need not necessarily be hydrocarbons. Different ways of molecular breakdown of such compounds may be reflected by the varying slope of the curves, which also seems to indicate, that the number of chemical individuals of fundamental genetic importance for paraffin waxes is limited.

The waxes differ in percentage in which the various structured paraffins are present in the mixture. Paraffins from distilled tar and synthetic waxes are chiefly straight chain and to a small part branched compounds, while the ceresinic waxes are more hydroaromatic. All groups occur in waxes from mineral oil, though the unbranched chains prevail in the lower cuts whereas they are getting scarcer in the higher ones. It

POSSIBLE GENETIC RELATION OF WAX FRACTIONS FROM ONE CUT  
TO A COMMON, COMPLICATED FUNDAMENTAL COMPOUND



can be derived from the graph in what cases such thermal treatment will substantially improve a paraffin, because the isomeric chains are split off with comparative ease, whereas no amelioration can be anticipated from waxes in which the cyclic components prevail. The graph can be divided into fields which reflect the crystallographic behaviour of the compounds, and some of the physical properties which are important in dewaxing e. g. solubility, the filtering properties or hardness.

The practical value of this way of plotting paraffin composition may be demonstrated on a few examples, in which for time saving reasons we also eliminated the separation to molecular weight, which is permissible only, if the molecular range is narrow.

1) A tar distillate from low temperature carbonization of German brown coal was to be dewaxed in two stages in a technical unit. The refinery had guaranteed that distillation be done under rough conditions (slight pressure) with regard to good filtering quality and production of commercial paraffin which could be bleached to water white color. Filtration rate in the first stage of the dewaxing plant was found 100 kilos per square meter per hour, which is pretty low for a well distilled lignite tar. The wax also needed considerable refining effort to obtain decent color and the refinery experts attributed those observations to a slight carry over of crude tar in distillation, which could neither be avoided nor be considered as objectionable within narrow limits.

The paraffin was therefore examined by fractionated crystallization such as described above. The result was:

Average Mol. W. of wax 380,  $D_{90}$  778, Melt. P. 56, 5°C

	Yield %	Melt. P.	Sp. G. 90°C	Class. No.
Fraction 1)	5	44	0,796	592
2)	15	48	0,782	276
70 % Iso 3)	25	54	0,777	108
4)	25	54	0,776	102
<hr/>				
30 % Straight 5)	11	61	0,775	16
6)	19	64	0,773	42

Allowing for the spread in molecular range it is feasible to regard 6 as normal wax. The separation revealed that the wax contained a preponderant quantity of branched paraffins. That proved that the tar had been distilled with caution. Actually it was admitted later that the distillation had been done in slight vacuum to avoid coke deposits in the stills. The new feed stock was distilled under rougher conditions and gave readily the expected high filtration rate for an expertly prepared tar distillate of 250 - 300 kilos/m<sup>2</sup>h. No difficulty was met in refining that wax to water white color.

II) In dewaxing a shale oil of Spanish origin the filtration rate was found to be 200 kilos per square meter per hour. Although this figure is satisfactory it was tried to increase it by various means like redistillation, slight chemical pretreatment, chilling and dilution, in order to cut filter surface down still further if possible. All efforts influenced filtration rate negligibly only. However, the answer was given by fractionation:

Average Mol. W. of wax 410, D<sub>90</sub> 765, Melt. P. 45°C

	Yield %	Melt. P.	Sp. G. 90°C	Class. No.
Fraction 1)	10	22	0,771	387
36 % Iso 2)	9	28	0,766	148
3)	17	34	0,766	124
4)	20	40	0,763	25
64 % Straight 5)	31	50	0,765	45
6)	13	62	0,772	30

The wax had already preferably straight chain character and no substantial improvement of filtration velocity could therefore be anticipated from distillation or chemical pretreatment.

III) A wax cut from Persian crude was dewaxed in the laboratory. The filtration rate was 80 kilcs per square meter and hour. The fractionated crystallization of the wax cake gave the following result, which is only little conclusive because the molecular range is too large.

Average Mol. W. of wax 500, D<sub>90</sub> 792, Melt. P. 58°C

	Mean Mol. W.	Yield %	Melt. P.	Sp. G. 90°C	Class. No.
Fraction 1)	580	13	1	0,831	4264
28 % Cyclic 2)	570	6	21	0,809	1922
3)	500	9	26	0,800	1450
35 % Iso ? 4)	450	18	38	0,795	924
5)	490	17	47	0,790	560
? 37 % Straight 6)	540	10	58	0,786	242
7)	490	27	70	0,780	50

Fraction 1) shows, that the wax contained oil by improper dewaxing conditions. The Class. No. 4200 indicates close proximity of that oil to waxes and indicates phase separation of the heavy ends of the long cut during dewaxing. Oil content for reason of poor washing would give much higher Class. No. for the given Mol. weight.

Fraction 2 and 3 disclose the presence of only little cyclic wax, which however may reduce filtration rate considerably. Fraction 4 - 7 indicate presence of a large percentage of the well filtering n-paraffins but the proportion iso - normal cannot be estimated from the mean Mol. W. of such a broad molecular range.

The next cut was taken a little shorter, eliminating partly the cyclic waxes for which dewaxing conditions can be more individually adjusted in heavy distillates or residues and the filtration rate climbed to 120 - 150 kg/m<sup>2</sup>h.

Fractionation and graphic plotting was useful in other cases to prove carry over of raw oil in distillation. This becomes evident if poor filtration rates are obtained for waxy stocks, for which the location in the graph indicates good filtering velocity.

The graphic survey will also be useful to find the most suitable application for a given wax, or to indicate how it should be further split up by distillation or dewaxing in stages, to get maximum economic benefit.

The candle maker prefers high melting straight chain paraffins, regardless of molecular weight, because they can easily be refined to water white color and have only little tendency to bend or mottle when perfectly free from oil.

The producer of fatty acids by wax oxidation asks for n-paraffins of a certain limited molecular range. Color does not matter in this case, but his second demand is absence of oil in the raw wax.



Branched and cyclic waxes are apt to produce synthetic lubricating  
oils in various ways. A very small oil content of the wax is not harmful  
in this case, but cuts of narrow molecular range lead to better results,  
especially if the lubricant is produced by way of chlorination and aluminum  
chloride treatment.

Plasticity is a desired quality for all waxes which are to give a  
protective cover to food and fruits, while hardness and the capability  
to absorb and hold a large quantity of solvent in even distribution is asked  
for the production of polishes.

The graph is useful to estimate in which percentage those qualities  
are present. It may also be of advantage if the question comes up to  
select a suitable raw material for the production of chemical individuals  
as a starting material for the chemical industry. It is quite possible, that  
compounds such as methyl-nonadecane or cyclo-octacosane are some day of  
importance as intermediates or starting materials for the production of  
synthetic chemicals. The described way of fractional separation and graphic  
plotting will then be of a fast method to test a large number of considered  
waxy raw materials.