CORRELATIVE INVESTIGATION OF BITUMENS

By

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Many tests are used for the scientific and practical characterization of bitumens. The number of these tests is so great that the results become rather limited, and often even a research specialist in this field is unable to correlate the data collected with much care and labour. Comparison of results obtained by various workers is extremely difficult because the tests generally used are not standardized but have a research character and are therefore quite different.

No doubt, the main difficulty originates in the very complicated structural buildup of bitumens, especially when investigations are carried out with respect to the single compounds. Bitumen, a substance that is composed of compounds of high molecular weights, and which is the result of a very complex geological history, contains a high number and variety of organic chemical compounds. Besides carbon and hydrogen, small quantities of sulphur, oxygen and nitrogen are present in it as heteroatoms, and, also in small quantities, sometimes in trace quantities only, metal-organic compounds are also to be detected.

The position becomes somewhat simpler if bitumens are classified according to groups of compounds that show definite physical and chemical characteristics and can be prepared by chemical solubility and adsorption methods. Groups of compounds defined on the basis of best known methods of group-analysis are the oils, the resins, the asphaltenes, the carbenes, the carboids, the acids, etc. Following the first up-to-date concept, presented by NELLSTEYN [1], of the colloidal structure of bitumens, quite a number of authors have proved it. Briefly, and much simplified, it can be said that the innermost core of the structure is made up of the so-called asphaltenes, that the resinous part surrounds this in the form of a defending colloid and peptizing it in different measures in the oily phase. Of course, the real picture is not as simple as that, and transitionary structures as functions of intermicellary forces, polarity, and molecular weights, of the compounds are probably more complicated depending on the effects of the physical state and the temperature of the system. On the basis of the state of peptization of the micelles, and of the structures evolved, authors distinguish sols and gels, and the most often transitionary sol–gel type. Naturally, since it is a substance of technological character even in a preponderantly scientific study, questions that pertain to raw materials production methods and application technology cannot be left out of consideration.

It is for about 15 years that we occupy ourselves with research in the field of bitumen structures and technologies. During this time we tried to fashion our research tools in such a way that having made a selection as to the best from the point of view of application, these we used consequently even when their number had to be increased. Thus a comparatively large and many-sided body of research experience has been accumulated. Part of the investigated bitumens originate from the Hungarian crudes of Nagylengyel, and since with these neither the raw material nor technological features vary to any great extent, they can also serve as a basis of comparison.

The aim of this paper is an attempt, by a retrospective survey, at bringing into correlation the data we have gathered in the course of investigations [3—19] that moved in various directions, and at drawing the appropriate scientific and technological inferences therefrom.

Table 1

Bitumen test-chart of a research institute

Density, d^{25}	
Softening point	
Ring and Ball method	°C
Kramer—Sarnow method	°C
Penetration at 0°C	0.1 mm
15°C	0.1 mm
25°C	0.1 mm
40°C	0.1 mm
50°C	0.1 mm
60°C	0.1 mm
Penetration index, P. I.	
Ductility at °C	cm
15°C	cm
25°C	cm
40°C	cm
Viscosity at °C	
°C	
°C	
°C	
°C	
°C	
Equiviscosity temperature	
at 20,000 cSt	°C
2,000 cSt	°C
200 cSt	°C
Fraas break point	°C
Stiffness modulus	
....°C .... sec	N/m^2
°C sec	N/m^2
°C sec	N/m^2
Loss on heating at 163°C	w.%
at higher temps	w.%

Softening point	
Ring and Ball method	°C
Rise of softening point	
Ring and Ball method	°C
Penetration at 25°C	0.1 mm
Increase of penetration	%
Ductility at ....°C	mm
Break point	°C
Rise of break point	°C
Loss on heating at 220°C	w.%
at higher temps.	w.%
Softening point	
Ring and Ball method	°C
Penetration at 25°C,	0.1 mm
Break point	°C
Flash point, open cup	°C
Fuming temperature	°C
Solubility in benzene	w.%
Insolubles in cyclo-hexane	w.%
Asphaltene, n-heptane	w.%
Flocculation behaviour	
(FR 10) .... %	xylene —
Sweat test (filter paper)	
Sulphur content	w.%
Paraffin	w.%
M.p. of paraffin	°C
Ash	w.%
Salt content	w.%
Neutralization number	mg KOH/g
Saponification number	mg KOH/g

For the purpose of comparison with practical data, we have retained the parameters of standard technological character but do not deal with their criticism or their scientific merit in great detail, neither do we wish to make a stand concerning their inclusion into standard specifications. Rather, we wish to illustrate the complexity of the present situation by the reproduction *(cf. Table 1)* of a test chart of a research institute [2]. The ultimate aim could be the development of a scientific classification system whereby also technological applicability could be predicted.

With a view to technical applicability, the aim of research is to help the manufacture of a product that

1. is resistant to effects of various strength and duration (e.g. to those of the loads of traffic in the case of bitumens in road construction) under extreme physical conditions like summer heat, and winter cold;

2. is resistant to the external chemical or physical ageing effects like aggressive groundwaters, climatic ageing;

3. maintains its adhesion properties, possibly under any condition.

With these features in mind, we have selected the principal lines of our research as follows.

We investigated
mechanical, rheological,
chemical and structural, and
structural ageing properties
of bitumens.

Though we did some research concerning adhesion characteristics, we will not discuss these here because adhesion is a function of the surface involved as well as that of the bitumen itself.

Studies concerning mechanics and rheology

No doubt, this is the group of properties for the testing of which most of the conventional and research methods are used, and the investigation of which had been carried out to the greatest extent. We too have done most of our work [3—19] in this field.

The problem of an adequate instrument restricts the choice of scientifically founded rheological methods. Bitumen too is a viscoelastic substance, its mechanical, or rheological properties vary accordingly. Due to their colloidal structure, most types of bitumen do not, at least below certain temperatures, obey Newton's law, i.e. shear stress is not proportional to shear rate. Thus, the viscosity of bitumens is not exclusively a function of temperature but also of conditions of flow. In this case we speak of a so-called "apparent" viscosity, keeping in mind that whereas this is a material constant of Newtonian liquids, it is a generalization in our case and serves to characterize flow phenomena, but cannot be considered as a specific and constant property of the substance. Consequently, for viscosity data that relate to bitumens, besides test temperature also shear rate values must be stated.

If viscoelastic effects are to be tested, an instrument is needed that enables the ratio of deformation to shear stress force to be measured as a function of time, i.e. the modulus of viscoelasticity or "stiffness", as POEL [20] has named it.

Typical "stiffness modulus" vs. load time curves are shown in *Fig. 1.* With loads of short duration elasticity effects are in evidence (horizontal part

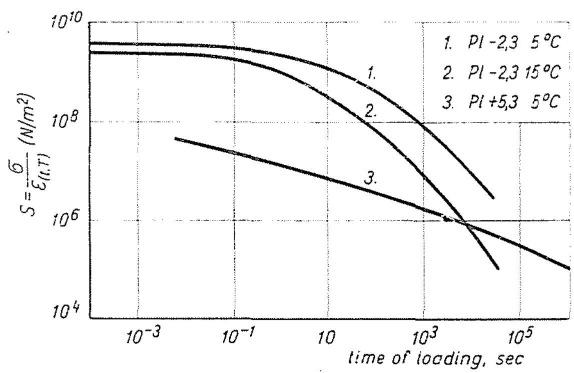

Fig. 1. Stiffness vs. time of loading curves characteristic for various bitumens

of the curve). With loads of long duration, viscous flow emerges independent of time (descent at 45° of the curve). The transition part is small, a rise in temperature causes a shift. Curve 3 represents the data of a blown bitumen; with these types "stiffness" is less subject to the effect of the time of loading, and prolonged elasticity effects come to the fore.

Omitting details of the question, we note that a similar curve appears in the case of bitumens of the same rheological character at the same temperature, reckoned from the softening point. On this basis a nomogram has been constructed [2, 20] and is used quite frequently to determine, from the known value of the softening point and from that of the penetration index, "stiffness" at a chosen temperature and time of loading, i.e. to determine "stiffness modulus".

In lack of an adequate instrument, we developed another form of rheological characterization.

To arrive at an informative characterization of a bitumen, hardness and rheological character data are necessary. Among the *conventional data,* hardness can be assessed, at a first approximation, by penetration. Rheological character can be deduced from the so-called penetration index [21, 4, 13], i.e. the ratio of penetration to softening point. A penetration index may be read off a graph, or can be calculated. Its value for bitumens is generally between −3 and +8. PFEIFFER, and VAN DOORMAL propose [21] a classification also characteristic of structure; according to this proposal bitumens with a penetration index of, or lower than, −2 are purely viscous or nearly so (so-called pitch types), those of a penetration index between −2 and +2 are the so-called sol types (most of the road building kinds), and those of a penetration index of +2 or higher are the gel type bitumens. According to our present knowledge of rheological phenomena this classification is obsolete and does not take into account the changes in the state of the system in function of temperature and time of loading, nevertheless the penetration index serves fairly well for a first approximation, and quite a number of nomograms have been constructed with the aid of which rheological features like the stiffness mentioned, ductility, Fraas break point, can be determined from softening point and penetration values, or from the penetration index.

In former communications [6, 10, 13] we have discussed our comprehensive research system, developed for the rheological assessment of Hungarian bitumens, including tests and evaluation methods. Among the mechanical properties, resistance to deformation and break strength may be emphasized as the most important. Resistance to deformation is a property of which the knowledge at maximum utilization temperature is the most important, break strength is the one of which the knowledge at minimum utilization temperature is the most important. Mechanical properties must be tested both for static and dynamic conditions because in practice projects are submitted to both these types of stress and to transitionary types between them.

We have dealt several times with the indirect characterization of resistance to deformation and of its correlation with structure. Data were measured at various temperatures with a Höppler type consistometer generally on samples at rest for 24 hours. For rheological characterization the so-called degree of complex flow was used with the restriction that measurements were carried out around the softening point and from 30 to 70°C below it, under circumstances defined for 10°C intervals. Average shear rate values were plotted in a log/log graph as the function of shear stress. Generally, measured values gave a straight line that could be described by the equation

$$M = \frac{F}{S^c}$$

where F = shear stress in dynes per square centimetre, S = shear rate in $\sec^{-1}$, and c = the slope of the line log S vs. log F referred to the shear rateaxis, i.e. the degree of complex flow. $M = F$ if $S = 1$. It was found that if the degree of complex flow was plotted as a function of the temperature reckoned from the softening point, a curve characteristic for the structure is obtained. TRAXLER [22] comments on the numerical values of the degree of complex flow as follows.

If this value is unity, then, structurally, bitumen is a Newtonian fluid, pitch-like, or a very well peptized sol. If this value is less than unity, then bitumen is a sol; around a value of 0.7 bitumen is a transition between sol and gel, and at around 0.5 bitumen is of a distinct gel structure.

Though in the course of these tests viscosity values can also be calculated, for the characterization of hardness the softening point or penetration values were retained.

Impact-bending strength was measured with a Schopper type hammer mechanism functioning on the Charpy principle, the method evolved by us is described in detail elsewhere [9]. A hammer mechanism of maximum 40 cm.kp work capacity was used on test pieces of 25 mm by 15 mm ∅ without incision; five such pieces were poured at one time. The required temperature of the test pieces was adjusted in an ultrathermostat, and the work expended on the breaking of the pieces was measured. *Tables 2, 3* and *4* show the

Table 2

Rheology and impact-bending strength of bitumens

Ser. number	Process	Softening point, °C	Penetration at 25°C, 0.1 mm	Penetration index	Asphaltene content, %	Degree of complex flow			
						10	20	30	40 °C
1.	Vac. dist. residue	33	300 f	—	17.6	0.78	0.81	0.84	—
2.	Vac. dist residue	39	249	+0.6	18.2	0.60	0.72	0.85	0.90
3.	Vac. dist. residue	52	76	+0.5	21.6	0.58	0.69	0.74	0.82
4.	Vac. dist. residue	56.5	53.5	+0.4	22.4	0.60	0.71	0.78	0.81
5.	Vac. dist. residue	70	23.0	+1.0	28.6	—	—	0.58	0.65
6.	Blown	88	22	+3.5	34.4	—	—	0.45	0.48
7.	Blown, from fuel oil	99	24.0	+4.8	38.8	—	—	0.35	0.37
8.	Vac. dist. residue	100	4	+1.9	33.8	—	—	—	—

40 f = above 40 cm.kp
T = broken, but could not be measured
R = cracked

results; Table 2 for Nagylengyel bitumens variously produced, Table 3 for distillation residue bitumens from various crudes, and Table 4 for bitumens from Romaskino crudes.

Before we discuss correlations, it is well to call to mind that bitumen is a viscoelastic substance the mechanical properties of which largely depend on temperature, load and time of loading. At high temperature and under great loads it is a Newtonian fluid, at low temperature and short time of loading it behaves as an elastic solid. In between, i.e. during use and under conditions for the determination of the degree of complex flow, their behaviour is very complex indeed, and, in most instances, depends on the degree of their deformation. If the data in Tables 2, 3 and 4 are considered, it will be seen that for bitumens of given hardness primarily the data about impact-bending strength measured above 0°C merit investigation; below 0°C the differences are rather blurred.

The least rigid and brittle are the Nagylengyel bitumens. On the basis of degrees of complex flow, bitumens from distillation residues show a transitionary structure within the temperature domain round about the softening point. However, when temperature is lowered, this turns into a gel structure and the curve of the degree of complex flow tends towards the 0.3 lower limit value. If blown, the Nagylengyel bitumens trend gradually to acquire a gel structure and, at values diminishing parallel to the degree of complex flow or at increasing values of the penetration index, the impact-bending strength

manufactured from Nagylengyel stock

flow					Work expended, cm.kp, on the breaking of test pieces with cross-section 25 by 15 mm							
50	60	70	80	90	+30	+20	+15	+10	+5	0	—10	—20
					°C							
—	—	—	—	—	—	—	—	—	—	40 f	15.5	10.5
—	—	—	—	—	—	—	—	40 f	R	23	9.5	8.5
0.85	—	—	—	—	—	—	40 f	31.5	14.5	10.5	7.5	6
0.84	—	—	—	—	40 f	R	23.5	18.5	10	8.5	7	6.5
0.74	0.82	0.85	—	—	40 f	T	19	13.5	8	7.5	6	5.5
0.55	0.60	0.65	0.70	—	—	40 f	T	25.5	16	11.5	6.5	6
0.40	0.42	0.43	0.45	0.49	—	—	40 f	T	17	7.5	7	6
0.60	0.67	0.73	0.75	0.80	12	8	7.5	7	6.5	6.5	6.5	5.5

values measured above 0°C and referred to the softening point become greater.

Referred to measure of blowing, degrees of complex flow of blown bitumens in function of temperature describe a flat curve. These types of bitumen contain a comparatively great amount of asphaltenes not very highly peptized.

Much more brittle and of little impact-bending strength also above 0°C are the distillation residue bitumens with low asphaltene content, i.e. those of Matzen, Romaskino and Tujmaz. The degree of complex flow around the softening point and in the temperature range investigated has a value of about unity. From the point of view of rheology, around their softening point

Table 3

Rheology and impact-bending strength of bitumens of

Ser. number	Origin	Softening point, °C	Penetration at 25°C, 0.1 mm	Penetration index	Asphaltene content, %	Degree of complex 10 °C	Degree of complex 20 °C
1.	Nagylengyel	52	76	+0.5	21.6	0.58	0.69
2.	Matzen	53	55	0	1 alatt	1	1
3.	Tujmaz	51	48	−1.0	12.3	0.8	1
4.	Lispe	55	80.5	+1.4	1 alatt	—	0.7
5.	Nagylengyel	53	68.5	+0.4	21.8	0.60	0.71
6.	Romaskino	53	39	−1.0	6.1	—	0.84
7.	50% Nagylengyel, 50% Romaskino	53	53	−0.3	14.5	—	0.75
8.	U.S.S.R.	50	54.5	−1.0	5.1	0.85	0.88
9.	50% Nagylengyel, 50% U.S.S.R.	52	55.5	−0.4	13.6	—	0.75

40 f = above 40 cm.kp
T = broken, but could not be measured
R = cracked

Table 4

Rheology and impact-bending strength of bitumens

Ser. number	Process	Softening point, °C	Penetration at 25°C, 0.1 mm	Penetration index	Asphaltene content, %	Degree of complex 10 °C	Degree of complex 20 °C	Degree of complex 30 °C
1.	Vac. dist. residue	53	39	−1.0	6.1	—	0.84	0.87
2.	Vac. dist. residue	50	54.5	−1.0	5.1	0.85	0.88	0.92
3.	Vac. dist. residue	38	237	−0.2	7	—	0.87	0.93
4.	Blown	55	57	−0.6	14.9	—	0.57	0.68
5.	Blown	64.5	26	+0.4	16.2	—	0.58	0.67
6.	Blown	68.5	22.5	+0.8	16.3	—	0.47	0.54
7.	Blown	82	12	+1.2	20.4	—	—	0.45

40 f = above 40 cm.kp
T = broken, but could not be measured
R = cracked

vacuum distillation residues from various origin

flow			Work expended, cm.kp, on the breaking of test pieces with cross section 25 by 15 mm²									
30	40	50	+30	+20	+15	+10	+5	0	−5	−10	−15	−20
			°C									
0.74	0.82	0.85	—	—	40 f	31.5	14.5	10.5	10.0	7.5	6.5	6
1	1	1	19	14	8	7.5	6.5	6	5	4.5	4.5	4
1	1	—	T	14	10.5	8	6.5	6	5.5	5	4.5	4
0.68	0.68	—	40 f	32	18	10.5	7.5	7.5	6	6	5.5	5.5
0.79	0.81	0.85	40 f	R	23.5	18.5	10	8.5	8	7	7	6.5
0.87	0.90	0.93	—	11.5	8	7	6.5	6.5	6	6	6	6
0.83	0.85	0.90	40 f	T	13	9.5	8	7.5	7	6.5	6.5	6.5
0.92	0.95	1	40 f	T	13	10	8	7	7	6.5	6	5.5
0.87	0.90	0.93	40 f	R	16	12	9	7.5	7.5	7	6.5	6

manufactured from Romaskino stock

flow					Work expended, cm.kp, on the breaking of test pieces with cross section 25 by 15 mm²							
40	50	60	70	80	+30	+20	+15	+10	+5	—10	—20	0
					°C							
0.90	0.93	—	—	—	—	11.5	8	7	6.5	6.5	6	6
0.95	1	—	—	—	40 f	T	13	10	8	7	6.5	5.5
1	—	—	—	—	—	—	40 f	16	9	7.5	7	6
0.87	—	—	—	—	—	R	15.5	10	8.5	7.5	6.5	6
0.75	0.87	0.87	—	—	40 f	T	15	9.5	8.5	8	7	6
0.71	0.79	0.84	—	—	40 f	25	13	8.5	8.5	7	6	6
0.49	0.56	0.61	0.65	0.68	—	11	9	8	7.5	7	6	6

they are close to a purely viscous fluid. An interesting fact is that the gel type Lispe bitumen that contains little asphaltene and shows a high paraffin value also exhibits greater impact-bending strength. Paraffin value is detrimental, mainly because it increases the change of viscosity as a function of temperature.

An amelioration of the lower impact-bending strength of Romaskino bitumens can be effected by admixing it with Nagylengyel bitumen. By blowing, also the asphaltene content of Romaskino bitumens can be increased and their gel character improved.

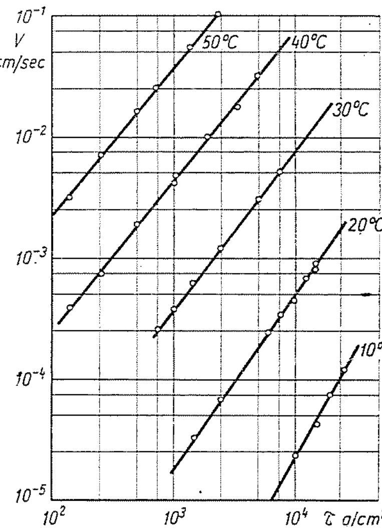

Fig. 2. Log shear rate (V) vs. log shear stress (τ) correlations at various temperatures, of bitumens of vacuum distillation residues made from Nagylengyel crudes

It is interesting to note that impact-bending strength data are different according to the structures tending to converge towards a common limit value. This seems to parallel the observed rheological phenomenon which consists in a convergence, when temperature decreases, of the degree of complex flow connected to gel structure becoming more pronounced, towards a limit value of 0.3. We may mention that this value of about 4...6 cm.kp at -20°C does not increase very much unless the bitumen is admixed with an additive substance, e.g. rubber grist.

To give an example of the application of our test method we present in *Fig. 2* a log/log graph of shear rate vs. shear stress plotted from data referring to a bitumen produced as a distillation residue of Nagylengyel origin. The graphically determined data of the function of degree of complex flow and temperature are collected in the fourth row of Table 2. On *Fig. 3* shear rate vs. shear stress of a bitumen blown from residual fuel of Nagylengyel at various temperatures is shown in a log/log plot. The data concerning complex flow data and impact-bending strength values are to be found in the seventh row of Table 2. Most informative and suggestive seemed to be the comprehensive form of presentation adopted e.g. in *Fig. 4* for a distillation residue of Romaskino crude, and blown bitumens.

For ageing tests, viscosities were measured with a sliding-plate and micro-film viscosimeter as constructed by LABOUT and VAN OORT [25]. A bitumen layer 40 to 100 microns thick was placed between two glass plates, the one fixed, the other movable. The displacement of the movable plate varies according

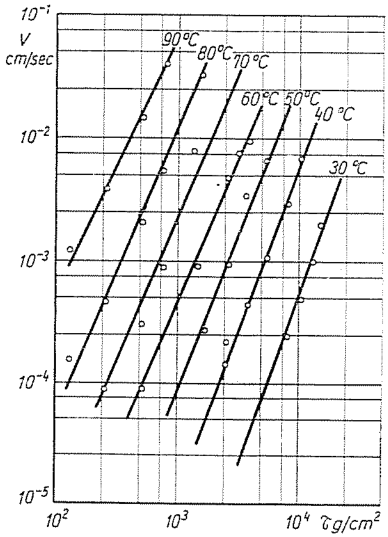

Fig. 3. Log shear rate (V) vs. log shear stress (τ) curves for various temperatures, of a bitumen blown from a Nagylengyel fuel oil

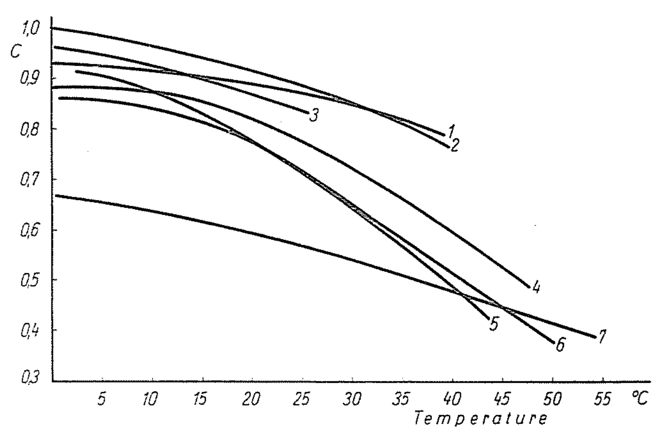

Fig. 4. Degree of complex flow of Romaskino bitumens as a function of the temperature reckoned from the softening point

to the load applied. A great advantage of this viscosimeter is that it requires a minute sample only; a disadvantage is that elasticity, thixotropy, etc., cannot be measured with it. Nevertheless it is a very useful tool in the estimation of the effects of ageing under various conditions because a thin layer of the sample suffices for the test to be carried out.

Chemical tests and the study of structures

The mechanical properties of bitumens depend mainly on their chemical or colloid chemical structure even if this correlation cannot in every instance be proved directly. However, there are authors who attribute but a subordinate role to the features of structure. For research of this kind a difficulty resides therein that the various groups interact and form a colloid chemical system among themselves. Thus, even if difficulties of identification could be overcome this would not suffice without the knowledge of how the groups identified affect each other structurally. The very detailed analytical data gathered with the help of the most up-to-date testing apparatus could not as yet be brought into adequate correlation with the properties of the binders.

The most useful methods have been those which split the bitumens according to chemically characteristic functional groups and try to predict the behaviour of bitumens when in use on the basis of the ratios and character of these groups. These analyses according to functional groups are now utilized to a much smaller extent than would be possible.

The main reasons for this neglect are the following.

1. Most of these methods are not simple enough for practical field work.

2. No method exists that has gained wide acceptance and is consistently applied.

To answer a demand as it arose here, we attempted the elaboration and introduction of a method that gives sufficient information about the structure of bitumens, yet does not involve too much laboratory work. The method of our choice is, as far as its essentials are considered, the same as that described by TRAXLER et al. [23].

For a detailed account of this method we refer to former communications [16, 17]. In essence it is the following. The lower molecular weight components are extracted from the bitumen sample with n-butanol, and the quantity of the so-called asphalt-like substances (I) is determined. The solvent is removed from the extract and the latter, in turn, is dissolved in acetone, cooled and filtered at $-23\,^{\circ}C$; the residue is then, according to the authors, fraction (III), i.e. that of the saturated compounds. The solution in acetone yields, when the solvent is removed, fraction (II) called that of the cyclic compounds. The designations (I), (II) and (III) are also those proposed by TRAXLER, since several authors did not accept his original ones.

Advantages of this method are the following.

The fractionation of bitumens into parts according to the main characteristic groups is made possible. It is simple, since two operations yield three fractions. On the basis of this fractionation into three parts the components of a bitumen can be plotted on a triangular chart, and with the help of such a chart a comparison of this bitumen with known types, guided by the published data

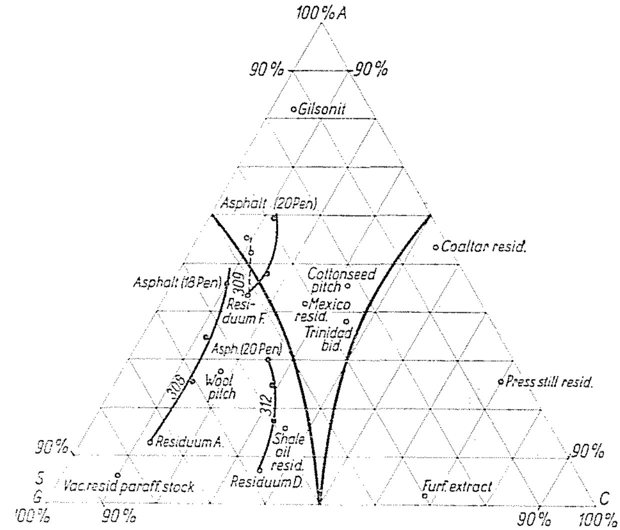

Fig. 5. Results, taken from the literature, of group analyses

of the latter, becomes feasible. Refractive indices, ultraviolet and infrared spectra to a certain degree reveal the chemical nature of the several fractions. With data about the degree of dispersion added [17] also the colloid state can be guessed at if the asphaltene content is known.

Results of our studies seem to suggest that they are in some correlation with colloid chemical, rheological and physical properties.

A further advantage is that this method yields results that are fairly reproducible.

In a calculation of the degree of dispersion, the amount of asphaltenes is subtracted from that of the asphalt-like compounds, the remainder is that of the heavy resins. To this is added the the quantity of the cyclic compounds, this sum is then divided by the sum of asphaltenes and saturated compounds. Amounts are expressed in per cents by weight. According to the theory that forms the basis of this method, it is mainly the saturated components which are responsible for the precipitation of the asphaltenes, in contrast to resin-like and cyclic components which exert a peptizing effect. From this it follows that the lower the degree of dispersion, the less is the peptization of asphaltenes, and the bitumen in question shows a gel structuree. If the degree of dispersion is high, then there is a sol structure present. *Fig. 5* is a suggestive form of the presentation of such results.

Various types of bitumen are plotted, according to their composition as stated in the literature, on a triangular diagram, and their position on it corresponds very well to the use the several types are put in practice, e.g. in road construction. A furfural extract, a typically aromatic product, is found in the

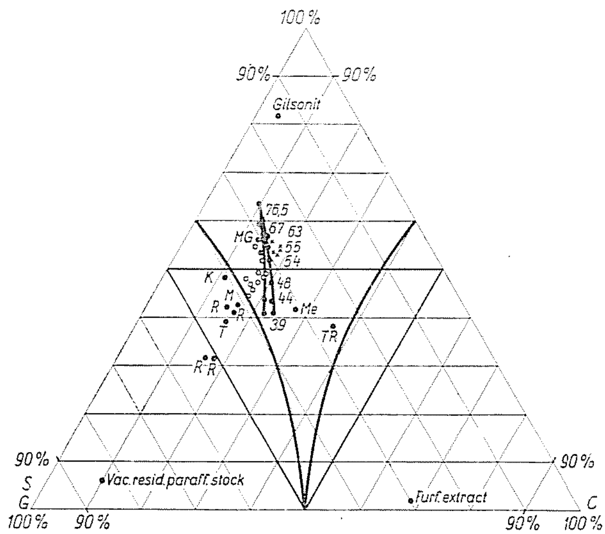

Fig. 6. Results of group analysis experiments ● Nagylengyel bitumen, vac. resid. × Nagylengyel bitumen, blown ○ Barabásszeg bitumen ●R Romaskino bitumen, vac. resid. ●M Matzen bitumen, vac. resid. ●MG Matzen bitumen, blown ●T Tujmaz bitumen, vac. resid. ●K Kardoskút bitumen, vac. resid. ●ME Mexico Res. ●TR Trinidad

corner of the diagram which is characterized by the preponderance of cyclic compounds. Gilsonite, known to contain much asphalt, emerges in the corner characterized by the preponderance of asphalt-like components. According to the opinion held by many authors, good bitumens fall into the middle or transitionary field. In these bitumens no single component type is predominant, thus their mechanical properties assume no extreme values. The known Mexican (Panuco) and Trinidad bitumens belong to this group.

On Figure 5 the effect of technological processes becomes apparent. It can be seen e.g. that during blowing the amount of asphalt-like compounds increases at the expense of saturated and cyclic compounds. The outcome of reduction in vacuo is similar, only the ratio of cyclic to saturated compounds is shifted. Of course, similar shifts occur in connexion with ageing.

Table 5

Study of the structure of bitumens from Nagylengyel and Barabásszeg

Ser. number	Mark of the sample	Softening point, °C	Penetration at 25 °C, 0.1 mm	Penetration index	Paraffin value %	Asphaltene		Separation by solvent								%-difference between asphalt-like components and asphaltenes contained by anal. benzine	Degree of dispersion
						by ether %	by anal. benzine %	Asphalt-like I, %	Cyclic II		Saturated III		Refined by acid, saturated			
									%	n_D^{70}	%	n_D^{70}	%	n_D^{70}		
1.	ND	38	279	+0.9	2.1	20.8	17.8	41.6	21.6	1.5501	36.8	1.5095	18.9	1.4950	23.8	0.83
2.	ND	48	105	+0.4	1.9	23.4	19.2	45.8	19.8	1.5582	34.4	1.5122	18.1	1.4960	26.6	0.87
3.	ND	56	55	+0.3	1.7	25.8	20.5	50.1	17.4	1.5569	32.5	1.5142	17.5	1.4992	29.6	0.89
4.	ND	62	37	+0.7	1.6	28.0	21.4	54.6	15.0	1.5590	30.4	1.5177	15.3	1.5043	32.3	0.91
5.	ND	75	18	+1.5	1.5	30.0	24.0	53.7	15.1	1.5671	31.2	1.5203	14.5	1.5082	30.6	0.83
6.	ND	83.5	8	+1.2	1.5	32.0	26.7	63.6	9.5	1.5773	26.9	1.5226	13.3	1.5122	36.7	0.88
7.	BD	76	32	+2.7	2.0	30.5	25.5	48.8	17.9	1.5467	33.3	1.5130	17.7	1.4950	23.3	0.70
8.	BD	84	27	+3.5	2.2	32.3	27.1	52.2	16.2	1.5560	31.6	1.5091	17.2	1.4920	25.1	0.70
9.	NF	85.5	25.5	+3.3	1.9	34.1	28.5	54.9	17.6	1.5482	27.5	1.5142	16.2	1.4928	26.4	0.79
10.	BD	84	39	+4.3	2.7	32.9	26.4	47.5	17.4	1.5477	35.1	1.5032	17.4	1.4870	21.1	0.63
11.	NF	89	40	+5.0	2.0	34.4	28.9	52.8	18.3	1.5497	28.8	1.5095	16.4	1.4935	23.9	0.76
12.	BD	115.5	16	+6.5	1.95	37.3	30.1	55.0	13.0	1.5655	32.0	1.5095	17.0	1.5655	24.9	0.61

ND = Nagylengyel, dist.; BD = Barabásszeg, dist.; NF = Nagylengyel, blown.

Correlation between experimental results of this method and the quality of bitumens

Results of our experimental work are presented in *Tables 5*, 6 and 8, and are plotted in a graph in *Fig. 6*. We think that for unknown bitumens this method gives pertinent information on the quality to be expected. This method enables us to make comparisons with types internationally known. It enables us also to estimate asphalt-like substances besides asphaltenes; the former include high molecular weight and resin components of which the quantity is considerable, especially in bitumens having little asphaltene content, e.g. in Matzen bitumens. Most likely these transitionary types of compounds are able to maintain a stable structure, and are easily converted into asphaltene by blowing. The difference between these bitumens and those of high asphaltene content consists therein that in the latter the conversion process had already occurred naturally. The uniformity of the refractive indices measured indicates uniformity of the separation and the selectivity of the method.

Application of this method facilitates the choice between bitumens blown and bitumens of dist. residuum. A selection of the best technological process will primarily be guided by the character of the raw material. If this is such that the rheology and structural composition of its product is not good, e.g. it shows a strongly negative penetration index, great sensitivity to temperature, low content of asphalt-like substances, and preponderance of the so-called saturated part, then, presumably, it will be more usefully applied after having been blown to a certain degree. The elucidation of the dependence of mechanical properties of bitumens on their structural features may eventually help the synthesis of bitumens. For there exist refinery wastes that are composed preponderantly of compounds of one group, e.g. various extracts, paraffinic residues, asphalt-propane residues. Compounded according to a suitable formula, these wastes could yield inexpensive bitumens. In *Figs 5* and *6* we marked the limit values originally proposed by SCHWEYER [24]. The triangle drawn in *Fig. 6* represents our proposal of categorization.

A survey of rheological data suggests that the best materials for use in road construction are the transitionary types and, to a certain degree, the asphalt-like bitumens. Later on, perhaps, it will be possible to set up certain group-composition specifications to characterize the good binders. From data referring to Nagylengyel and Barabásszeg bitumens (cf. Table 5), and on the basis of *Fig. 6*, it can be stated that from the point of view of group composition the Nagylengyel bitumen falls into that part of the diagram where, according to the opinion of several authors, the best bitumens belong. The effect of technologies can be traced to a certain measure by this method. When bitumens made as vacuum distillation residues with different

Table 6

Study of the structure of bitumens of various origin

Ser. number	Mark of the sample	Softening point °C	Penetration at 25°C, 0.1 mm	Penetration index	Paraffin value %	Asphaltene		Separation by solvent								%-difference between asphalt-like components and asphaltenes contained by anal. benzine	Degree of dispersion
						by ether %	by anal. benzine %	Asphalt-like I, %	Cyclic II		Saturated III		Refined by acid, saturated			
									%	n_D^{70}	%	n_D^{70}	%	n_D^{70}		
1.	Romaskino	43	170	+0.4	2.3	9.65	4.35	31.6	17.4	1.5740	51	1.5276	19.3	1.4988	27.25	0.79
2.	Romaskino	49	57	—0.1	2.1	8.63	3.6	31.5	16.0	1.5740	52.5	1.5280	18.3	1.5012	27.9	0.78
3.	Romaskino	53	39	—1.0	2.1	12.7	6.2	41.5	16.3	1.5860	42.2	1.5240	17.8	1.5008	35.3	1.06
4.	U.S.S.R.	50	54.5	—1.0	2.2	9.3	5.1	42.7	14.1	1.5822	43.2	1.5225	19.3	1.5012	37.8	1.03
5.	Matzen	51.5	56	—0.5	<1	2.35	0.25	42.8	16.3	1.5685	40.9	1.5140	18.2	1.4942	42.5	1.39
6.	Matzen	93	7	+1.9	<1	24.6	17.0	56.6	12.9	1.5681	30.5	1.5122	16.1	1.4930	39.6	1.10
7.	Tujmaz	52.5	39.5	—1	2.0	8.4	7.0	39.4	15.4	1.5726	45.2	1.5182	13.8	1.5038	32.4	0.92
8.	Dutch Shell	111	29.5	+6.3	1.4	28.8	24.9	43.2	20.5	1.5475	36.3	1.4927	14.7	1.4816	18.3	0.63
9.	Kardoskút	58.5	49	+0.4	6.4	—	16.6	48.6	11.0	1.5488	40.6	1.4976	18.4	1.4858	32.0	0.75

softening points are compared, it is found that in the softening point range from 40 to 75°C the amount of asphalt-like components increases by about 20 per cent. In the case of blown bitumens, the relative increase of asphalt-like components within the same range of softening points is less, and so is the decrease of the amount of cyclic components. Even less is the change of the amount of saturated compounds. The degree of dispersion is practically uniform with the rise of the softening point brought about by distillation process. This fact is in good accord with rheological properties. However, it is surprising that distilled samples from Barabásszeg in tests behaved like the highly blown samples: their degree of dispersion was the lowest.

Group analyses of other types of bitumens. From the point of view of the future of the Hungarian bitumen industry, among the bitumen samples tested the analysis of Romaskino type samples was of interest. Here some deviations between results were found. In *Table 6,* the degree of dispersion of samples Nos 3 and 4 was high, and also the amount of asphalt-like components was quite great. As was found by component-analyses, Romaskino type samples Nos 1 and 2 had lower degrees of dispersion, in accord with penetration index values characteristic for rheological behaviour. The asphaltene content of the Matzen bitumens is rather low but increases considerably when blown. It is also interesting that the amount of heavy resins, shown by the difference, and greatest in Matzen bitumens among those tested up to now, together with the refractive indices of the fractions, did not change during blowing. The highest degree of dispersion was found in samples of bitumens made from Matzen vacuum distillation residues.

Durability tests of bitumen

Experiments were carried out to ascertain the durability of bitumens, and to elucidate its dependence on chemical composition and on rheological data. In the course of their application and use, bitumens are exposed to effects, e.g. of oxidation, light, heat, photo-oxidation, water, adsorbents, mechanical load and microbial life, that may bring about significant chemical changes or structural modifications. Within this domain, intensity and ratio of single factors may depend on the conditions of use. Thus for bitumens used for roofing climatic, for those in underwater insulation mechanical, chemical and microbiological, for those used in road paving, again weathering, adsorption, etc. factors in interaction will be of paramount importance.

These influences usually cause changes like hardening, increased brittleness, reduced adhesion, etc. which formerly were considered as being mainly due to the volatility of the lighter components; to-day, however, it is known that molecular rearrangement is one of the causes of reversible hardening, greater viscosity due to cooling being another, while irreversible hardening is one consequence of chemical changes like polymerization, oxidation, and of the subsequent rearrangements of colloidal structures, etc. Thus it is possible that a bitumen of originally good mechanical properties is of low application value nevertheless, because it is easily oxidized. Therefore, by our experiments we made an attempt at a clarification, mainly on the basis of rheological properties, of the dependence of durability on chemical composition.

A former communication [19] describes our methods, and refers to the literature on this subject. The most costly method mentioned in the literature is the construction of an experimental road section. However, this implies that favourable or detrimental effects of construction technology, of extreme climatic conditions, of extreme loads, obscure the picture. A further difficulty is the very long time of research. On a smaller scale but still rather costly and lengthy are the Weather-O-meter tests proposed by STRIETER: these take from 30 to 60 days, give reproducible results, but then their relation to practical conditions is doubtful.

Therefore, various laboratory methods for the ageing of bitumens were evolved of which the following are best known.

1. Oxygen absorption (or bomb) method by ANDERSON.
2. Oxidative hardening index by WILKINSON et al.
3. Thin-film method of LEWIS and WELBORN, i.e. the B. P. R. thin-film test. Now the ASTM D—1754 specification.
4. Microfilm ageing test, or the so-called Shell method, at present an ASTM-Recommendation.
5. Oxidation method by EBBERTS.
6. Combined microfilm test of GALLAWAY and EBBERTS.

Items 3 and 4 have gained wide acceptance, and we also used these.

The so-called loss of heating test as practised here, was developed, in essence, from the method of LEWIS and WELBORN; this test was also resorted to in our studies.

The most accurate evaluation of ageing phenomena is possible when thin films of the sample are used. The introduction of the sliding-plate microviscosimeter *(cf. Fig. 7)* enabled us to examine such small samples. This instrument was designed by LABOUT and VAN OORT [25]. Thin-film oxidation has been proposed by GRIFFIN et al. [26].

The essence of the method is as follows. From the bitumen sample a film, 9 to 11 microns, is prepared between two parallel glass pates. When the plates are separated, an about 5 micron film is obtained and put for 2 hours, at 107°C, into a drying oven for oxidation on a sample-holder revolving at 5 to 6 r.p.m. Following this operation, the bitumen sample is detached from the glass plate and placed between the plates of the viscosimeter mentioned. The viscosity of the original sample and that of the aged sample is measured at 25°C. With the help of the graphs obtained also the degree of complex flow was determined. The ageing index we calculated from viscosity data determined graphically at a shear rate $5 \cdot 10^{-2} \cdot \left(\frac{v_2}{v_1}\right)$. A similar $\frac{c_2}{c_1}$ ratio was calculated from the degrees of complex flow before (c_1) and after (c_2) ageing.

Indirect methods for the prediction of the useful life of bitumens

In our communication mentioned [19], we collected from the literature those results of experiments or studies which can be brought into correlation with the number of cycles measured on a Wheater-O-meter. Such are the

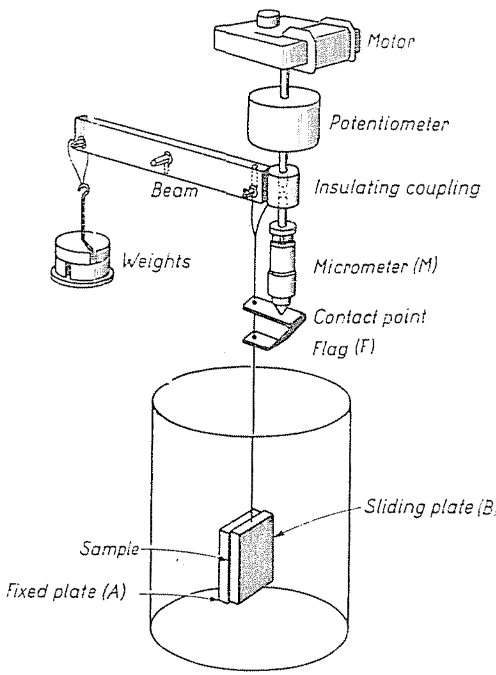

Fig. 7. Schematic drawing of a sliding-plate micro-viscosimeter

viscosity of the maltene phase, infrared spectra of thin bitumen films, carbonyl-index, asphaltene filterability, asphaltene content, dispersion factors according to MARTEOS and according to TRAXLER. Among these we determined the two last and the asphaltene content, and we also calculated the critical solubility factor. Results obtained in connexion with ageing tests are shown in *Tables 7 and 8*; in Table 7 the results of thin-film ageing tests, and in Table 8 those of chemical analyses and stability tests are presented. These Tables, given as examples, contain results on samples that can be tested, both before and after ageing, at 25°C.

Table 7

Results of thin-film ageing tests of bitumens

Serial No. of test	1.	2.	3.	4.	5.	6.	7.	8.
Designation of the sample	Nagylengyel, vac. dist. res.	Nagylengyel, vac. dist. res.	Nagylengyel, vac. dist. res.	Nagylengyel, vac. dist. res. to be blown	Nagylengyel, blown sample No. 4	Nagylengyel, sample No. 5 blown further	Romaskino, distillation residue	Romaskino, distillation residue
Data of the untreated bitumen Penetration at 25°C, 0.1 mm	227	204	146	over 360	234	155	190	83
Softening point, Ring and Ball method, °C	41	41.5	44.5	37.5	40	46	43	48
Viscosity, at 25°C, v_1, in cP, measured in a sliding-plate viscosimeter, at $5 \cdot 10^{-2}$ sec^{-1} shear rate	$9.5 \cdot 10^7$	$8.0 \cdot 10^7$	$1.8 \cdot 10^8$	$1.9 \cdot 10^7$	$3.2 \cdot 10^7$	$7.4 \cdot 10^7$	$8.0 \cdot 10^7$	$3.5 \cdot 10^8$
Degree of complex flow, c_1	0.73	0.73	0.75	0.78	0.75	0.63	0.93	0.87
After the determination of the thin-film ageing (Shell) index, at 107°C, 5 to 6 r.p.m., for 2 hours, film thickness 5 microns								
Viscosity, at 25°C, v_2, in cP, measured in a sliding-plate viscosimeter, at $5 \cdot 10^{-2}$ sec^{-1} shear rate	$4.0 \cdot 10^8$	$3.8 \cdot 10^8$	$6.5 \cdot 10^8$	$2.6 \cdot 10^8$	$2.5 \cdot 10^8$	$3.65 \cdot 10^8$	$1.5 \cdot 10^8$	$6.6 \cdot 10^8$
Degree of complex flow, c_2	0.44	0.58	0.41	0.41	0.46	0.45	0.62	0.47
Viscosity ageing index, a. I. $= \frac{v_2}{v_1}$	4.22	4.75	3.61	13.69	7.81	4.93	1.88	1.88
Degree of complex flow ageing index, CI $= \frac{c_2}{c_1}$	0.60	0.77	0.55	0.53	0.61	0.71	0.67	0.54

Table 8

Group-analysis results and colloid stability data of bitumens

Serial No. of test	1.	2.	3.	4.	5.	6.	7.	8.
Designation of the sample	Nagylengyel, vac. dist. res.	Nagylengyel, vac. dist. res.	Nagylengyel, vac. dist. res.	Nagylengyel, vac. dist. res. to be blown	Nagylengyel, blown sample No. 4	Nagylengyel, sample No. 5 blown further	Romaskino, distillation residue	Romaskino, distillation residue
Data of the untreated bitumen								
Penetration at 25°C, 0.1 mm	227	204	146	over 360	234	155	190	83
Softening point, Ring and Ball method, °C	41	41.5	44.5	37.5	40	46	43	48
Asphaltene content, % — determ. with anal. benzine	16.2	16.6	17.8	16.6	17.9	19	4.4	6.8
Asphaltene content, % — determ. with ethyl ether	20.1	22.9	24.3	19.8	22.7	24.2	11.3	12.3
Paraffin value, %	2.1	2.1	1.9	2.3	2.3	2.2	2.3	2.5
Fraction I, %	42.9	41.7	43.9	37.2	38.8	39.7	32.0	32.1
Fraction II — %	23.4	23.6	22.0	24.1	23.2	22.0	20.3	22.8
Fraction II — refraction at 70°C	1.5480	1.5540	1.5528	1.5513	1.5450	1.5480	1.5650	1.5855
Fraction III — %	33.7	34.7	34.1	38.7	38.0	38.0	47.7	45.1
Fraction III — refraction at 70°C	1.5090	1.5090	1.5180	1.5000	1.5174	1.5134	1.5243	1.5049
Fraction I — Asphaltene I, %	25.9	23.7	25.5	20.8	20.9	20.7	27.6	16.0
Degrees of dispersion acc. to TRAXLER	0.99	0.95	0.96	0.81	0.79	0.75	0.92	0.92
Degrees of asphaltene dispersion, acc. to MARTENS	0.61	0.62	0.61	0.55	0.59	0.59	0.71	0.71
Critical solubility factor	7.95	7.94	7.95	8.03	7.97	7.97	7.81	7.81
Inhomogeneity test in solvent mixture:								
0% xylene + 100% n-heptane	—	—	—	—	—	—	3333	3333
5% xylene + 95% n-heptane	—	—	—	—	—	—	2333	2222
10% xylene + 90% n-heptane	—	—	—	—	—	—	1222	1222
15% xylene + 85% n-heptane	3333	—	—	—	—	—	1112	0112
20% xylene + 80% n-heptane	2333	2223	3333	3333	3333	3333	0000	0000
25% xylene + 75% n-heptane	0113	0002	1113	1223	1223	2223	—	—
30% xylene + 70% n-heptane	0000	0000	0000	0000	0000	1111	—	—

For the method of the modified inhomogeneity spot-test we refer to the literature. We may mention that according to our experience nearly the same inhomogeneity values pertain to bitumen types, and to technologies generally, irrespective of hardness, but if the instability indicated by the spot-test also appears at higher xylene ratios then thermal effects, contamination by a foreign substance, and change of basic materials may be suspected. In the last two cases the shift can also appear in the instability pertaining to lower xylene concentration.

Again, the degree of complex flow, determined by the sliding plate test as shown in Table 7, points to the transitionary sol—gel character of Nagylengyel bitumens and to the sol structure of Romaskino bitumens.

Among the ageing-test results in Table 8, the ageing index of sample No. 4 is conspicuous in so far as this value could not be expected on the basis of loss on heating tests. By blowing, ageing properties seem to improve. The general experience is that the ageing index of bitumens from Nagylengyel distillation residues is a value around 4. Romaskino types have their index around 2. This index, as found in the literature, which falls between about 2 and 15, in this respect Nagylengyel bitumens occupy quite a good position, Romaskino bitumens doing even better. This is reassuring in the case of Nagylengyel bitumens, because in loss on heating tests the change of the conventional data is rather great, though within the tolerance limits. The degree of complex flow, characteristic of structural changes with age, does not present such a uniform picture, neither could we distinguish sharply enough one type of bitumen from the other. It seems that structural changes due to ageing and those due to temperature decrease are similar, i.e. that bitumens originally of a sol type assume gel structure during ageing, whereas bitumens of the transitionary and gel types alter their character slightly. On the basis of chemical and stability data we might say the following. In the case of all the bitumens studied, asphaltene content, the softening points also taken into account, remains below the level deemed to be unfavourable from the point of view of useful life. Paraffin content goes beyond the prescribed 2 per cent maximum only in a few instances and by a very small margin even then. The higher paraffin contents of Romaskino bitumens is what can be expected on the basis of group-composition. Again we refer to *Figs 5* and *6*, according to which also the data shown in Table 8 point to the fact that Nagylengyel bitumens are close to the central section marked by Mexican and Trinidad bitumens.

Conclusion

The most important statements arrived at can be summarized thus.

Rheological character. Bitumens can be fairly well characterized by conventional data that define hardness, as e.g. by the softening point or penetration, by the penetration index, further by the degree of complex flow determined at softening point and in 10°C intervals of the range between 30 to 70°C below softening point, finally by impact-bending strength figures measured in the range between 0 and 20°C. Transitionary and gel type bitumens, besides being less sensitive to temperature, show greater impact-bending strength in the temperature domain above 0°C than do sol type bitumens. Of course, the temperature for which comparisons were made was calculated from the softening point. Below 0°C, differences were blurred, impact bending strength sank to about the same level for all the bitumens tested. Amelioration was possible only through addition of e.g. rubber grist. From the rheological point of view, Nagylengyel bitumen behaved well, Romaskino bitumen proved more brittle and more sensitive to temperature.

Group composition analysis. It is also advisable to qualify bitumens on the basis of group composition. Our choice of method proved to be advantageous, it furnished reproducible results. Group composition of Nagylengyel bitumens were found to be very like that of the best bitumens of Mexico and Trinidad; the composition of Romaskino, Matzen and Tujmaz bitumens were found to be less favourable, due e.g. in Romaskino bitumens to higher paraffin content and lower ratio of asphalt-like components.

Stability of colloidal structure. For the characterization of colloid stability, degrees of dispersion of asphalten according to MARTENS, and according to TRAXLER, were used, and our own inhomogeneity test developed from the spot-test described by OLIENSIS. Generally, these tests give results also characteristic for raw materials; the degree of dispersion, according to a number of authors, affects the useful life of bitumens. The values obtained are quite good and suggest a long useful life. Based upon degree of dispersion, Matzen bitumens are to be expected to last the longest.

Durability. For this, test the so-called Shell method, recommended also by the ASTM, was used, and a sliding-plate viscosimeter served for evaluation. Ageing was carried out at 5 micron film-thickness, and the viscosimeter mentioned proved to be best for the handling of such small samples. The ageing index of bitumens used in known experimental road-sections falls between 2 and 14. Therefore the value 4 measured for Nagylengyel bitumens, and value 2 measured for Romaskino bitumens can be regarded as very good indeed, even by world standards.

As shown in this paper, a great number and variety of experimental approaches were utilized in this evaluation of bitumens. Therefore it might be reassuring both for bitumen producers and bitumen users that the generally known very good quality of the Nagylengyel bitumens is proved and confirmed by this work, i.e. that, on account of their mechanical, rheological, structural and ageing properties these bitumens rank among the very best. Not so reassuring, however, is the fact that our experts do not pay enough attention to the application of Romaskino bitumens which, though less good on mechanical, rheological and structural points, yet promise to have the longest useful life. We avail ourselves of this opportunity to press for large-scale application tests of Romaskino bitumens here, so much the more as in the future Romaskino crude will be an important raw material of the Hungarian petroleum industry.

Summary

By the use of a wide array of experimental techniques we have attempted a complex evaluation of the various properties of bitumens. Over and above the study of conventional data, the most important questions tackled were the following: Rheological character, group-composition, stability of the colloidal structure and durability of bitumens.

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