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Research Department
African Explosives and Chemical Industries Ltd.
P.O. Northrand
Union of South Africa

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THE INFLUENCE OF RUBBER ON THE BRITTLENESS AND VISCOSITY OF BITUMINOUS MATERIALS

By P. MASON*, E. N. THROWER and L. M. SMITH†

The brittleness and resistance to deformation of rubber/bitumens and of sand asphalts made with rubber/bitumens have been investigated and compared with results obtained with similar materials not containing rubber. The brittleness tests were carried out by subjecting the materials to an imposed rate of tensile strain at 0°, the stress and strain being measured throughout the test. The deformation characteristics were measured in a wide-gap concentric-cylinder apparatus, the tests on bitumens being conducted at 25° and those on sand asphalts at 45°. The results show that the incorporation of rubber produces a material which displays, under the test conditions used, a marked increase in resistance to deformation, simultaneously with a reduced brittleness at low temperatures. It is concluded that, although some free rubber is clearly present as a separate phase, the modification of the normal bitumen properties is due at least in part to dispersion of the rubber on a molecular scale.

Introduction

Investigation of the influence of small proportions of rubber on the mechanical properties of bituminous materials has been carried out over the last twenty-four years in the Netherlands, the U.K. and, more recently, in the U.S.A. A review of this work up to 1951 has been given by de Decker & Nijveld[1] and more recent accounts, including the American work, are quoted in the bibliography.[2–5]

From this emerged the suggestion that admixture of rubber can both increase the hardness and decrease the brittleness of a bituminous material. Either of these effects can be achieved *separately* by changing the grade of bitumen; a *simultaneous* alteration in these properties, however, would indicate a qualitative change conferring features valuable in most forms of road construction.

The suggestion did not, however, find general acceptance, largely because the evidence behind it was empirical and, in part, subjective, without any evident bearing on the mechanical conditions experienced in the road. The present authors have re-examined the idea in terms of absolute physical properties, viz. viscosity and brittle extensibility, these being measured under conditions reasonably similar to those believed to obtain with road surfacings.

The comparison between bitumen and rubber/bitumen was investigated first, although here there was no information on the stresses or strains which are imposed in practice and the test

* Present address: British Rubber Producers' Research Association, Welwyn Garden City, Herts.
† Present address: British Rubber Development Board, Mark Lane, London, E.C.3

conditions were therefore arbitrary. Normal and rubberized sand asphalts were then studied and as it was possible to estimate typical strain conditions in asphalt road surfaces, particularly those relating to brittle fracture, greater emphasis was laid on the tests made on these materials. As shown below, the general conclusions applied equally to the bitumens and to the asphalts.

Experimental

Materials

Relatively hard and soft bitumens (25 pen. and 60 pen.) were used for the control materials, and the rubberized bitumens were prepared as described below. Technical details of all materials used are given in Appendix I.

Each bitumen was heated and stirred at 170° for 1 h. with sufficient unvulcanized rubber powder for the final product to contain 5% of rubber hydrocarbon. The choice of this particular set of conditions resulted from preliminary work in which samples of the 170° rubber/bitumen blend taken at ½, 1 and 2 h. showed little difference in viscosity and elastic recovery when tested at 25° in the Lee & Warren viscometer.[6]

Two compositions of sand asphalt were used. These were of the general type specified in the British Standard for hot-rolled asphalt[7] and comprised sand, limestone filler and binder, i.e. bitumen or rubber/bitumen, in the following proportions:

	% by absolute volume		% by weight	
	Mix type A	Mix type C	Mix type A	Mix type C
Sand	65·3	62·1	75·8	74·2
Filler	12·0	11·4	14·2	13·9
Binder	22·7	26·5	10·0	11·9

The mixes differ only in solid/liquid ratio, the proportion of filler to sand being constant.

Test conditions

The viscosity and brittle extensibility measurements were carried out at temperatures typical of British road surfaces in summer and winter respectively. It is permissible to base the comparisons on measurements at only single temperatures because the temperature coefficient of viscosity of a bitumen is not appreciably altered by the addition of rubber,[8] and the mechanical properties are not greatly influenced by temperature changes inside the brittle region. The test temperatures used, viz. 45° and 0°, appeared from measurements made by the Road Research Laboratory to be reasonable seasonal extremes. For the bitumens and rubber/bitumens, however, it was experimentally simpler to measure the viscosities at 25° and this temperature was therefore used for these materials.

The other important factor to be related to road conditions was rate of strain. For the bitumens and rubber/bitumens no information was available on values appropriate to practical conditions and the values used for these materials were somewhat higher than those used for the sand asphalts, where a design basis was available.

For the sand asphalts the rate of strain in viscous testing was of the order of 10^{-5} sec.$^{-1}$, following an analysis given by Nijboer.[9] The rates of strain used in brittle testing were based on the analysis, given by Fox,[10] of stresses in a typical road structure. This indicated that at low temperatures, the maximum tensile stress developed in the wearing courses may be from 1 to 3 times the applied normal stress. Taking a contact pressure of 10^7 dynes/sq. cm. (Nijboer,[9] p. 12) and assuming a stiffness modulus of 3×10^{11} dynes/sq. cm., a linear strain of approximately 10^{-4} is implied. Under moving traffic the strain at a point increases from zero to a maximum and back to zero in a time within the range 0·25 to 0·01 sec.[11] so that the mean rate of strain is between 10^{-3} and 10^{-2} sec.$^{-1}$. Brittleness was therefore measured as the extensibility in a simple extension test conducted in this range of rate of strain.

Test methods

(1) *Viscosity.*—All viscosity measurements were carried out using the wide-gap plastometer described in a previous paper.[12] This is a rotating-cylinder instrument with an annular gap several inches wide which can be used to provide a series of shear/time curves at different constant

values of shearing stress. Shear/time curves for the bitumens at a particular value of shear stress are shown in Fig. 1. The effect of the addition of 5% of rubber is to produce a large increase in viscosity of a bitumen, as can be seen also in Table I.

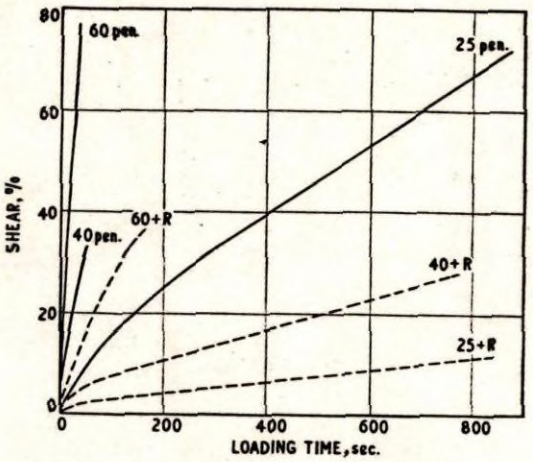


FIG. 1. *Shear/time curves for binders of bitumen and bitumen containing* 1% *rubber* (*R*)
temperature = 25°
shear stress = 5×10^4 dynes/sq. cm.

Table I

Effect of rubber on viscosity

Binder	Composition	Viscosity, poises		Test conditions
		without rubber	with rubber	
60-pen. bitumen		$3{\cdot}1 \times 10^6$	25×10^6	Temperature: 25°; Shear stress: 5×10^4 dynes/sq. cm.
40-pen. bitumen		$9{\cdot}4$	167	
60-pen. bitumen	Asphalt mix A	$1{\cdot}3 \times 10^9$	$7{\cdot}1 \times 10^9$	Temperature: 45°; Shear stress: $1{\cdot}2 \times 10^5$ dynes/sq. cm.
,,	Asphalt mix C	$2{\cdot}0$	12	
25-pen. bitumen	Asphalt mix A	$6{\cdot}2 \times 10^9$	68×10^9	Temperature: 45°; Shear stress: $3{\cdot}6 \times 10^5$ dynes/sq. cm.
,,	Asphalt mix C	$6{\cdot}6$	108	

Sand–asphalt specimens were formed by compacting a pre-determined weight of material to approx. $\frac{1}{2}$ in. thickness using a ram at 800 lb./sq. in. Rubberized and control materials were pressed at different temperatures to obtain similar degrees of compaction, the A-type mixes containing approximately 10% of voids and C-type mixes approximately 6%. Binder specimens were formed by pouring the hot binder into the annulus against a cover plate, coated with a silicone grease, which was removed when the specimen had cooled.

Some of the shear/time curves for the softer asphalts at a stress of $1{\cdot}2 \times 10^5$ dynes/sq. cm. and for the harder materials at $3{\cdot}6 \times 10^5$ dynes/sq. cm. are shown in Figs. 2 and 3 respectively. These have the same form, both in shear and in tension, as the deformation/time curves published by Lee & Markwick,[13] and it is evident that the addition of rubber in all cases produced a marked hardening of the material. Values of viscosity at a given shearing stress computed from the linear portions of the curves are listed in Table I. These values appear considerably lower than those of Nijboer[9] for similar materials, but an exact comparison is not possible because the maximum stress used in the present measurements was only about 1/100th of the minimum stress used by Nijboer; extrapolation of these data over this range, on the assumption that the viscosity of such materials is independent of the stress, would clearly be unjustifiable.

As the deformation/time curves obtained from the plastometer are derived from experimental data by graphical differentiation, individual observations do not appear on the graphs and the internal accuracy of the experiments is not apparent. In Fig. 2, the deformation curves from duplicate tests on mix A6 (A-type mix with 40-pen. bitumen) are shown. These were carried out partly to bridge the gap between A1 and A2 and partly as a check on the reproducibility of the tests.

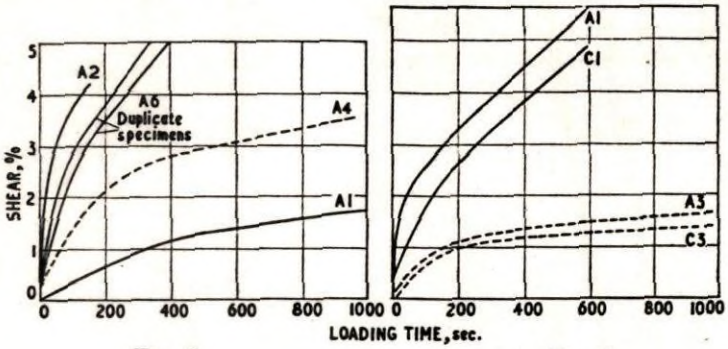


FIG. 2.

FIG. 3.

FIG. 2. *Shear/time curves for sand asphalts*

temperature = 45° shear stress = $1 \cdot 2 \times 10^5$ dynes/sq. cm.

No.	Binder
A1	25 pen.
A2	60 pen.
A4	60 pen. + rubber
A6	40 pen.

FIG. 3. *Shear/time curves for sand asphalts*

temperature = 45° shear stress $3 \cdot 6 \times 10^5$ dynes/sq. cm.

No.	Binder
A1	25 pen.
C1	25 pen.
A3	25 pen. + rubber
C3	25 pen. + rubber

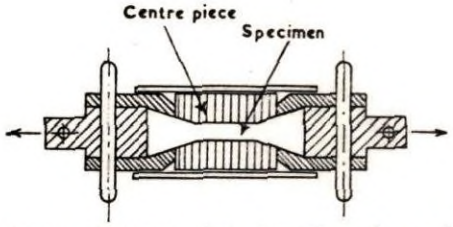


FIG. 4. *Sectional view of specimen in mould ready for testing*

(2) *Brittle extensibility of bitumens.*—To avoid the difficulties involved in demoulding binder specimens, a new method has been developed in which the test is carried out with the mould in position. Fig. 4 shows the experimental arrangement. Two end-pieces of the type used by Rigden & Lee,[14] together with the brass centre-piece, slide freely in the outer brass tube. The centre-piece is amalgamated internally with mercury to prevent adhesion. To prepare a specimen, the assembly is held vertically with the upper end-piece removed and hot binder is poured in to the required level. When cool, the end-piece is inserted and pinned in position and the outer tube is lubricated with a thin silicone oil.

Testing was carried out in a constant-temperature room, maintained at 0° by means of a Hounsfield tensometer. The ' fixed ' grip of the tensometer was attached to a stiff leaf spring on which rested the probe of a dial gauge. Tests with a spring balance served to calibrate the dial gauge in terms of load on the spring. A complete record of behaviour during a test was then obtained by photographing the dial gauge simultaneously with a stop-watch by its side at 64 frames per second. The movement of the dial gauge defined the start of loading and the instant of break, and also the extension of the specimen, in conjunction with the stop-watch readings and the crosshead speed. In this way the stress/time and strain/time curves from the start of loading up to the instant of fracture were obtained.

In the early stages of extension, the strain/time curves showed a lack of smoothness, probably caused by binding in the tube; in general, however, the rate of strain rose from about 4×10^{-2} sec.$^{-1}$ to 7×10^{-2} sec.$^{-1}$. Only a few tests have been made with this technique, but each of the four binders used in the sand asphalts has been examined and the extensibilities are given in Table II. The measured tensile strengths of these binders ranged from about 30 to 44 kg./cm.^{2}

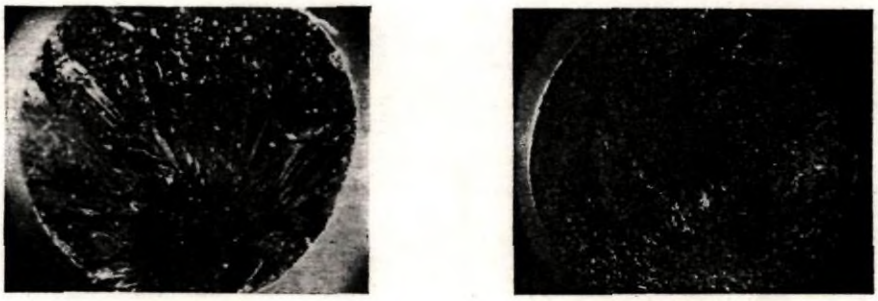
In addition to the quantitative differences shown in the Table, striking qualitative differences were observed in the appearances of the fractured surfaces. All specimens broke at right angles to the applied tension but whilst the normal bitumens showed characteristic features of glass-fracture surfaces,[15–17] viz. an area of ' mirror ' surface bounded by a ' frosty ' zone which

Table II

Effect of rubber on brittle extensibility at 0°

Composition	Extensibility × 10^{-4}		Standard error of means
	without rubber	with rubber	
60-pen. bitumen	450	730	40
25-pen. bitumen	330	770	
60-pen. bitumen–sand–asphalt	13	17	0·7
25-pen. bitumen–sand–asphalt	6	9	

led into an area of radiating 'hackle', the specimens containing rubber had a matt surface with none of the glassy characteristics. The contrast between the two types of surface is shown in Fig. 5.



(*a*) (*b*)

FIG. 5. *Fracture surfaces of binders (diameter of cross-section 3 mm.)*
(*a*) 25-pen. bitumen: the dark circular zone is a highly reflecting surface
(*b*) 25-pen. bitumen with rubber

(3) *Brittle extensibility of sand asphalts.*—Brittle testing of sand asphalts was also carried out by a tensile test, but the specimens used had a square cross-section some thirty times greater in area than that of the bitumen specimens and were produced in open moulds by rolling, in order to obtain adequate compaction. The method of gripping the ends of the specimens, however, did not preclude a small amount of relative movement between the specimen surface and the grip, so that it was no longer possible to deduce the strain in the specimen from the displacement of the grips.

Instead, the strain in the specimen was measured directly, together with the tensile force, throughout the test. A schematic diagram of the arrangement used is shown in Fig. 6. The specimens were extended in a lever balance testing machine having a maximum crosshead speed of 6 in./min. The dumb-bell shaped specimens were 10 in. long, $\frac{3}{4}$ in. thick, and 2 in. wide at the ends, tapering to $\frac{3}{4}$ in. wide over the centre 8 in. They were moulded at temperatures between 100° and 140° and compacted by 24 passes of a 300-lb. rolling load. The temperature of compaction was varied on the basis of preliminary trials, so that the rubberized mixes had substantially the same proportion of voids as their normal counterparts.

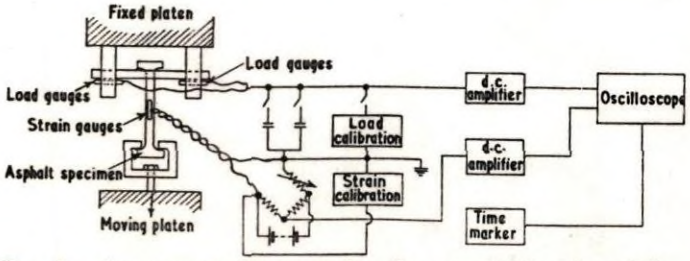


FIG. 6. *Arrangement for measuring the extensibility of asphalt at 0°*

As the testing machine had of necessity to be operated at room temperature, the specimens were coated with about ¼ in. of powdered ice and were stored at 0° up to the time of test. Measurements with embedded thermocouples showed that this technique gave satisfactory control, i.e. within 1°, provided that the layer of ice was retained on the specimen throughout the test.

The strain in the specimens was measured using two 1000-ohm wire strain gauges, 2 in. long, cemented with Araldite to the centre of the two flat faces and connected in series to form one arm of a bridge. The output from the bridge was fed to a d.c. pre-amplifier and thence to one beam of a double-beam d.c. oscillograph, the combination having a gain of about 4500. The load developed by the specimens was measured with two quartz piezo-electric gauges resting on a stirrup attached to the upper (stationary) platen of the machine. Each gauge supported one end of a steel bar forming the upper specimen grip, so that the total load was divided between them. The two gauges were connected in parallel, and their output taken via another d.c. pre-amplifier to the other beam of the oscillograph. The gauges were shunted with a high capacity (2 or 4μF) which, in conjunction with the high-input impedance (cathode follower) of the pre-amplifier, gave a time-constant more than adequate for the work.

To calibrate the strain-measuring circuit before each test a 1MΩ resistor was switched across the strain gauges, thus producing a known resistance change in this arm of the bridge. Calibration of the load-measuring circuit before each test was obtained by applying a voltage from a potential divider which had been previously standardized in terms of spot deflection on the oscillograph using a proving ring in place of the specimen.

The movements of the oscillograph spots during a test were recorded on a film moving at 5 in. per second and a time-scale was obtained by blacking out the traces every 0·02 sec. using a suitably shaped pulse derived from the mains.

Each test provided curves of tensile stress and strain in the material from the start of loading up to the instant of fracture. Typical results are shown in Fig. 7. These show that the rate of strain was not constant but increased steadily throughout the test, presumably owing to relative

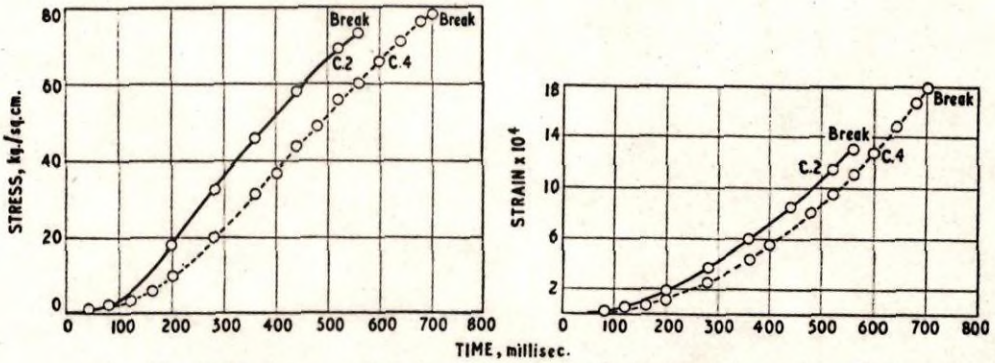


FIG. 7. *Typical stress and strain curves from tensile fracture test on sand asphalts*

No.	Binder
C2	60 pen.
C4	60 pen. + rubber

movement between the grips and the ends of the specimen. Different strain/time curves were obtained for different specimens, but analysis of the complete set of results, based on the time to reach an arbitrary strain, showed no significant difference between the materials being compared. It was therefore possible to make direct comparison between the extensibilities on the basis of an imposed rate of strain increasing from zero to about 3×10^{-3} sec.$^{-1}$ over a period of about half a second.

Preliminary examination showed that the differences in extensibility between A- and C-type mixes having the same binder were small, the corresponding means varying by about 7%. The values from corresponding A and C materials were therefore pooled. The A mixes contained slightly more air than the C mixes, on average 6·5% against 4%, so that all materials contained approximately the same proportion of solid. In this way, four sets of results were obtained relating to sand asphalts based on hard and soft bitumen with and without rubber. Each material

was represented by nine specimens and the extensibilities given in Table II are each the mean of nine tests. The tensile strengths of the materials under the experimental conditions used were also evaluated and these results are given in Table III.

The significance of the observed differences in extensibility was assessed by analysis of variance using a simple cross-classification test to test the effects of (1) bitumen hardness and (2) addition of rubber. The increases in extensibility produced by decreasing the hardness or by the addition of rubber were both found to be highly significant (i.e. at the 1% level).

Table III

Tensile strength of sand asphalts at 0° in kg./cm.²

Bitumen hardness	Means of nine tests		Standard error of means
	Control	With rubber	
25 pen.	44	67	5
60 pen.	53	80	

Discussion of results

Comparison of Tables I and II shows that rubber can both increase the hardness and reduce the brittleness of a bituminous material under conditions reasonably representative of those obtaining in a road surface. Graphical illustration of the point is provided by Figs. 8 and 9.

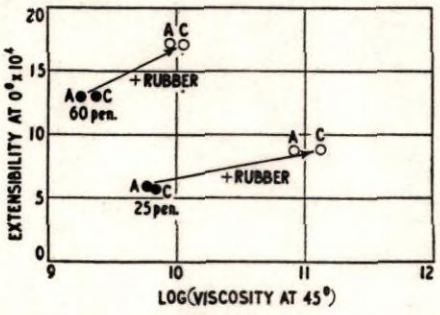


FIG. 8.

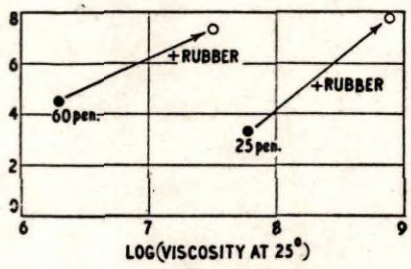


FIG. 9.

FIG. 8. *Effect of rubber on the viscosity and extensibility of sand asphalts*

FIG. 9. *Effect of rubber on the viscosity and extensibility of bitumens*

Discussion of the mechanism of these effects turns first on the nature of the rubber/bitumen blend. If the rubber powder were simply dispersed in the bitumen, then the increase in viscosity as given by the Einstein relation would be approximately 12%. The considerably greater increases shown in Table I may be explained on the basis of either (1) van Rooijen's concept that the rubber particles swell to about five times their initial volume by preferential absorption of the lighter fraction of the bitumen, so that the residual bitumen will itself increase in viscosity, or (2) the assumption that the rubber is dissolved, or at least dispersed on a molecular scale, in the bitumen.

Application of van Rooijen's work to the present materials indicates that the blend of 5% rubber in 60-pen. bitumen is physically a dispersion of 25% by volume of swollen rubber particles in a continuous phase consisting essentially of 25-pen. bitumen. Using the viscosity data of Table I, this would suggest that the viscosity of the rubberized 60-pen. bitumen should be in the region of 140×10^6 poise instead of the observed value of 25×10^6. It appears, therefore, that van Rooijen's hypothesis is not entirely true, and it has not been found possible at this Laboratory to obtain direct evidence of the swelling of rubber in bitumen to the extent suggested.

In view of the high initial molecular weight of the rubber (of the order of one million), dissolution of the rubber in the bitumen could account for the observed increase in viscosity. A series of observations using a microscope with a heated stage showed rubber particles in contact with bitumen, swelling, bursting their boundaries, and flowing into the bitumen until the system was optically homogeneous under time and temperature conditions less severe than those used in the present work. On the other hand, identifiable particles of rubber were found in the rubber/bitumen blends used here, and it is suggested as a working hypothesis that a

rubber/bitumen blend be considered as a dispersion of fine, possibly swollen, rubber particles in a solution of rubber in bitumen: the hardening effect is then due primarily to the molecular dispersion of the rubber in the bitumen.

The origin of the effect of rubber on brittleness is obscure, not surprisingly in view of the lack of understanding of fracture processes in solids generally. Qualitatively, however, a significant clue is provided by the comparison of the fracture surfaces discussed above and illustrated by Fig. 5. The glass-like nature of the bitumen is reduced by the presence of rubber and it is feasible that this results from a modification of the elastic properties of the material so that the ability to develop high stress-concentrations at cracks or other flaws is greatly reduced. Many visco-elastic tests have shown that rubber does produce considerable changes in the elastic properties of bitumen, but as there is no method at present available of relating the observations to tensile-failure properties, they have not been quoted in the present paper.

On the microscopic structural scale it is clear that either the presence of undissolved rubber particles in the neighbourhood of flaws or the modification of the bulk elastic properties by the molecular dispersion of rubber could account for the observed change in brittle quality.

In the former case the rubber would be acting purely as a mechanical filler and, as Lee & Rigden[14] have shown, the presence of inelastic filler in amounts of the order of 5% by volume can produce considerable changes in the tensile properties of bitumen, but inspection of the fracture surfaces of such a material revealed glass-like characteristics quite distinct from the rubber/bitumen surface in Fig. 5. Furthermore, when the rubber/bitumen shown in Fig. 5 was fractured at −75° the surface resembled that produced at 0°. At the lower temperature any free rubber particles would be quite rigid and inelastic, so that the action of the rubber in reducing the glassy character of the bitumen is quite distinct from that of a filler.

It may be concluded that the effects of rubber on the viscous and brittle properties of bitumen are due, at least in part, to molecular dispersion of the rubber in the bitumen.

Appendix I

Properties of materials used

(i) *Bitumen*

Bitumen No.	1	2	6
Origin		Middle East	
Penetration (I.P. method 49/53)	25	60	40
Asphaltene content (per cent)	20	12½	17

(ii) *Rubber:* Pulvatex unvulcanized natural-rubber powder, containing 60% rubber and 40% mineral filler

(iii) *Limestone filler*

Density	2·70 g./c.c.
Bulk density in benzene	0·75 g./c.c.
Dry compacted voids	0·31
Specific surface (air permeability)	0·29 m.²/g.

(iv) *Redhill sand*

Passing No. 25 B.S. sieve: % by wt.	100
,, 52 ,, ,, ,, ,,	52
,, 72 ,, ,, ,, ,,	23
,, 100 ,, ,, ,, ,,	8
,, 200 ,, ,, ,, ,,	0

Acknowledgments

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Road Research Laboratory
Harmondsworth, Middx.

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THE MICRODETERMINATION OF DISSOLVED OXYGEN IN WATER. V.* DEVELOPMENT OF A SELF-TESTING AND FULLY COMPENSATING ANALYTICAL METHOD

By E. C. POTTER and J. F. WHITE†

An ion-exchange technique is shown to be effective for removing interference by ferrous ion in the Winkler reaction. A referee method for the determination of dissolved oxygen in water is described incorporating full allowance for interfering substances and tests for bias and precision. The precision of one estimate of dissolved oxygen by the method is $\pm 0{\cdot}0015$ p.p.m.

Introduction

The preceding paper in this series[1] has demonstrated that the Winkler reaction is suitable in principle for the determination of dissolved oxygen in water even at concentrations below 0·001 p.p.m. The procedure there described can obviously form the basis of an analytical method, but as already pointed out in Part I[2] no such method may claim reliability or success for very low concentrations unless it embodies both correction for interfering substances and means of testing when this correction is effective. The existence of interference, the effects of which are uncorrected by the Schwartz–Gurney ' reversed-reagents ' technique, complicates the analytical application of the Winkler reaction. The present paper examines this application and describes the development of procedures now incorporated in the referee method for dissolved oxygen adopted by the Central Electricity Authority.

Experimental

I. Uncorrected interference

(a) *Occurrence*

Uncorrected interference is operating in a dissolved-oxygen analysis when a grossly inaccurate result is obtained in spite of the use of a ' blank ' correction, e.g., the ' reversed-reagents ' technique. The first paper of this series[2] showed that ferrous ion in the water being analysed is one source of uncorrected interference. There are other sources, but these would not be expected in almost deoxygenated waters such as boiler feed waters, so that our chief concern is with ferrous interference.

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† Present address: Atomic Energy Research Establishment, Harwell