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ESTIMATION OF THE TOTAL AND EFFECTIVE RUBBER CONTENTS OF RUBBER-BITUMENS

By **W. SZATKOWSKI**

Methods are described for estimating the total content of natural (unvulcanised) rubber in a rubber–bitumen and the effective rubber content; the latter is defined as the concentration of a standard rubber which would give a specific viscosity equivalent to that of the rubber in the test sample. The total rubber content is calculated from the iodine value of a solution, in carbon tetrachloride, of the acetone-insoluble fraction of the rubber–bitumen. The effective rubber content is determined by a measurement of the specific viscosity of a benzene solution of the acetone-insoluble fraction of the rubber–bitumen. The effective rubber content has been shown to be related to the elastic recovery of the binder.

Both analytical techniques have been used to follow the effect of heating on rubber–bitumens and recommendations are given on the conditions of temperature and duration of heating in the preparation of rubberised binders for road use.

Introduction

The addition of small quantities of elastomers, notably natural rubber, to road bitumen modifies its physical properties in such ways as would be expected to improve its performance in road surfacing materials. For example, the temperature-susceptibility of the bitumen is reduced, and a degree of elasticity is imparted. A programme of co-operative research is being undertaken by the Natural Rubber Bureau and the Road Research Laboratory to examine these properties and to see how far they are in fact reflected in improved road performance.

Adequate dispersion of natural rubber in bitumen can be achieved only by a period of heating at temperatures above 120°, and, for nearly all uses of rubber–bitumen, further heating is involved; during this further heating, however, the rubber will be degraded, the amount of decomposition depending on temperature and time. Because the desirable properties that the rubber adds to the bitumen depend both on the quantity and on the molecular state of the rubber, it is important to know to what extent the rubber has been affected by the heat treatment. For example, it is known that in some instances binders have been heated to such an extent that the rubber was rendered completely ineffective.

Unfortunately, no convenient and reliable methods have hitherto been available for estimating how much rubber a binder contains and in what condition the rubber is present. This article describes methods recently developed in the course of the co-operative research mentioned above. These methods measure:

(*a*) the total rubber content, i.e. the amount of rubber polymer of all molecular weights;

(*b*) the effective rubber content, i.e. the amount of a standard rubber which when added to bitumen will give the same specific viscosity in benzene solution as the test sample.

Analytical considerations

The greatest practical difficulty of estimating the amount of rubber in bitumen is that it is impossible to recover unchanged unvulcanised rubber once it has been dispersed in the bitumen. A well-known method of Heurn & Begheyn,[1] later improved by Salomon *et al.*,[2] converts the rubber to insoluble ebonite from which the bitumen is removed by solvent extraction; this method, however, gives very little indication of the condition of the rubber and is tedious for routine analysis.

The problem of estimating the amount of rubber in bitumen, by either chemical or physical means, is complicated by the presence of the bitumen itself which may react with the chemical reagent or interfere with the physical measurement. The influence of the bitumen will vary, depending on its source and viscosity. The methods of test finally adopted were: (*a*) the iodine value for the total rubber content, and (*b*) the specific viscosity as a function of molecular weight for the effective rubber content. During the present research it was found that the variability introduced by the bitumen could largely be eliminated by extracting from the rubber–bitumen that portion which is insoluble in acetone; this fraction contains all the rubber even when it has been so degraded that it has lost the power to add any elastic properties to the bitumen. Further, the acetone-insoluble fractions of the different bitumens examined in the early stages of the work reacted almost identically to the chemical and physical processes used in the tests; this fraction constitutes about 20—30% of the bitumen. In later stages of the research, it was found that some variation did occur among the acetone-insoluble fractions of different bitumens. The effect of this variation is negligible on the specific viscosity, but may be significant on the iodine value. Thus a blank determination of iodine value on a sample of unrubberised bitumen is recommended for an accurate estimation of the total rubber content. If a sample of bitumen is not available, a good approximation may be obtained using the iodine values given later in this paper.

Experimental

If the rubber-bitumen to be examined has already been mixed with aggregate to produce a road-surfacing material, it must first be recovered by extraction with solvents, using the technique described by Green;[3] toluene, benzene or methylene chloride may be used for extraction. Mineral filler should be removed by centrifuging the solution before the solvent is evaporated.

In practice it is more convenient to precipitate the acetone-insolubles than to extract the solubles. The analysis therefore consists of adding acetone to a solution of rubberised bitumen in a hydrocarbon solvent, removing the precipitate, and estimating (*a*) the degree of unsaturation in the acetone-insoluble fraction, and (*b*) the specific viscosity of a solution of the fraction in benzene. The former test gives the total rubber-hydrocarbon content; the latter, by comparison with a standard rubber solution, the effective rubber content.

The rubber–bitumen (15·0 g.) is dissolved in benzene (90 ml.) in a flask fitted with a mechanical stirrer. To this solution acetone (180 ml.) is then added over a period of 1 min. with vigorous stirring. The resulting mixture is continually stirred for another 15 min. during which time the acetone-insolubles should coagulate and adhere firmly to the walls of the flask. The supernatant liquid, which is now clear and of a deep red-brown colour when viewed in transmitted light, is poured off and rejected. The precipitate is taken up in a little methylene chloride and transferred to a tared 100-ml. beaker in which it is evaporated to constant weight on a steam bath.

(a) *Determination of degree of unsaturation (iodine value)*[4, 5]

All the reagents used in the following analysis are of Analar grade. The acetone-insoluble fraction (200—400 mg.) is dissolved in a mixture of 60 ml. of carbon disulphide and 20 ml. of carbon tetrachloride in a 250-ml. conical flask with a ground-glass stopper.

Wij's iodine solution (20 ml. of approx. 0·2 N) is then added by pipette, and the mixture is set aside in the dark for 20 min. at 18—20°. Forty ml. of 5% aqueous potassium iodide solution are then added and the excess iodine is back-titrated with a standard 0·1 N-thiosulphate solution. The end point (with starch added towards the end) is usually clearly visible in the aqueous phase. If, however, it is obscured by the formation of an emulsion, distilled water should be added. The iodine value is conventionally expressed in cg. of iodine which react with 1 g. of sample.

The total rubber content of the original rubber–bitumen is then calculated from the formula:

$$\mathrm{R}_{\text{total}} = \frac{(I - I_{\mathrm{B}}).\ 100n}{374 - I_{\mathrm{B}}}\ \%\ \mathrm{w/w}$$

where n is the fraction of the rubber–bitumen insoluble in acetone, I its iodine value and I_B the iodine value of the acetone-insoluble fraction of the bitumen alone. (The iodine value of pure rubber is 374.)

The value of I_B determined for a number of samples of Venezuelan bitumen ranged from 40 to 42. Middle East bitumens were more variable in this respect and I_B values as high as 58 were recorded although the majority of samples had values between 41 and 43. The I_B value for the acetone-insoluble fraction of the benzene-soluble extract of Trinidad Lake asphalt was 39·5. Where possible, the value of I_B for the type of bitumen present in the samples should be determined. Where this is not possible, the figures quoted above may be used to obtain an approximate value of the rubber content.

In determining the iodine value, it should be noted that both bitumen and rubber also give rise to substitution values, and to avoid abnormally high results the stated reaction time and temperature (20 min. at 18—20°) must not be exceeded.

(b) *Determination of the specific viscosity of the acetone-insoluble fraction*

The acetone-insoluble fraction (1·0—2·0 g.) is dissolved in benzene to give a 5% solution w/v. This is filtered into an Ostwald capillary viscometer and the viscosity of the solution is determined in a constant-temperature bath at 25·0 ± 0·1°.

The specific viscosity (η_{sp}) of the solution is calculated from the conventional formula:

$$\eta_{sp} = (t_1 - t_2)/t_2$$

where t_1 is the time taken by the standard volume of solution to flow and t_2 is the time taken by the standard volume of solvent.

The acetone-insoluble fraction of rubber-free bitumen gives values of η_{sp} ranging from 0·30 to 0·40 for a 5·0% solution in benzene. The average value of η_{sp} for this fraction is therefore taken as 0·07 for every 1% concentration of the fraction in benzene.

Any variations in the above value arising from differences between the bitumens are ignored because the effect of the acetone-insoluble portion of the bitumen on the specific viscosity of the benzene solution is small in comparison with the effect produced by a high polymer such as rubber.

The specific viscosity of a polymer is not in theory proportional to its concentration, but for the purpose of this analysis a linear relation is assumed for the limited range of concentrations used and for the degree of accuracy required. From a series of experiments with undegraded rubber, using benzene containing 5% of the acetone-insoluble fraction of bitumen, the following relation was deduced between the change in specific viscosity and the change in concentration of rubber:

$$\triangle(\%\ \text{rubber in benzene}) = 0{\cdot}167\ \triangle(\eta_{sp})$$

The term 'effective rubber content' is defined as the concentration of undegraded rubber that must be added to the bitumen to give the same η_{sp} as the test sample. As a standard, undegraded rubber is assumed to have an average molecular weight corresponding to an intrinsic viscosity in benzene $[\eta] = 400$ ml./g. This is an arbitrary choice in that it is a practical value representative of commonly available rubbers rather than the highest value attainable with natural rubber. It is possible, therefore, for the effective rubber content to be higher than the total amount of rubber added. As will be shown later, this does not invalidate the relation between the effective rubber content and the change in elastic properties of the binder.

If n is the acetone-insoluble fraction of the rubber-bitumen and if p (% w/v) is the concentration of the fraction in benzene giving a specific viscosity of η_{sp}, then the effective rubber content is given by:

$$R_{eff} = \frac{16{\cdot}7}{p}(\eta_{sp} - 0{\cdot}07p)n\ \%\ \text{by wt.}$$

Because of the non-linearity of the relation between specific viscosity and rubber concentration, particularly at the higher rubber concentrations, it is advisable to choose such a value of p that the actual amount of rubber in the benzene solution for which η_{sp} is measured, does not greatly exceed 0·5% w/v. For the great majority of rubberised bitumens, which usually contain only a small proportion of added rubber, a convenient value of p is 5·0% w/v. The formula then reduces to:

$$R_{eff} = 3{\cdot}35(\eta_{sp} - 0{\cdot}35)n\ \%\ \text{by wt.}$$

Practical applications

The performance of rubberised binders in full-scale road experiments has not yet been fully evaluated, because most of the experiments have not been in progress for a sufficient length of time. It is impossible, therefore, to correlate the performance of rubberised binders used in full-scale road experiments with the effective rubber content as determined by the method described above.

Laboratory experiments have been carried out, however, in which rubberised binders were heated at temperatures likely to prevail in full-scale work. The elasticity of the binder, as measured in a coni-cylindrical viscometer,[6] was found to be related to the effective rubber content (see Fig. 1). It was also found, as shown in Fig. 2, that the temperature of heating influences both the time taken to reach the maximum effective rubber content and the period during which this maximum is maintained. The fall in unsaturation as indicated by the iodine value, shown in Fig. 3, suggests various changes in the structure of the polymer, such as cross-linking and degradation, taking place simultaneously but at different rates.

The curves of Fig. 2 are of value for determining the duration of heating permissible at the

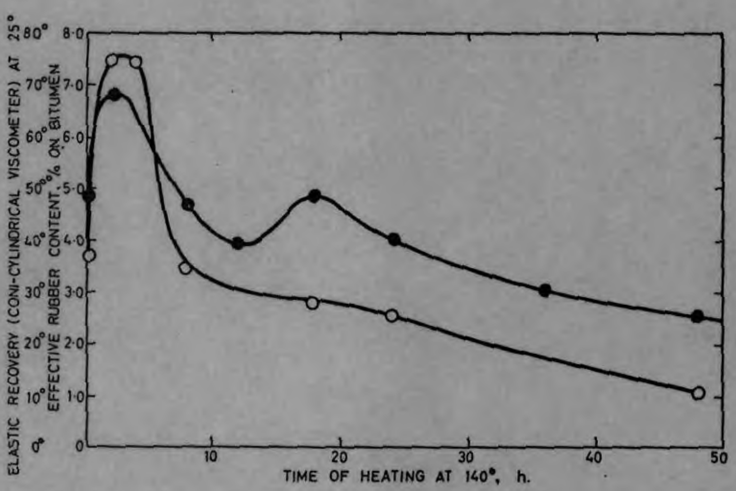

Fig. 1. *Relation between elastic recovery* (○) *and effective rubber content* (●)

Composition of material by wt. 50/60 pen. bitumen 77%, kerosene 19·25%, rubber 3·75%

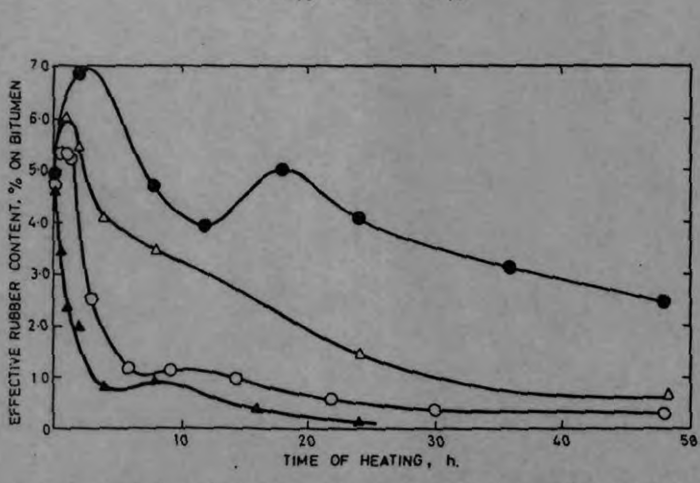

Fig. 2. *Variation of effective rubber content with time and temperature of heating*

● 140° △ 160° ○ 180° ▲ 200°
(material as in Fig. 1)

temperature to which any particular type of road material is heated. Thus, for instance, a cutback rubber–bitumen for surface dressing may be kept for many hours at 140° before any decrease in its effective rubber content can be detected: on the other hand, a mastic which has to be heated to about 200° may lose its effective rubber very quickly.

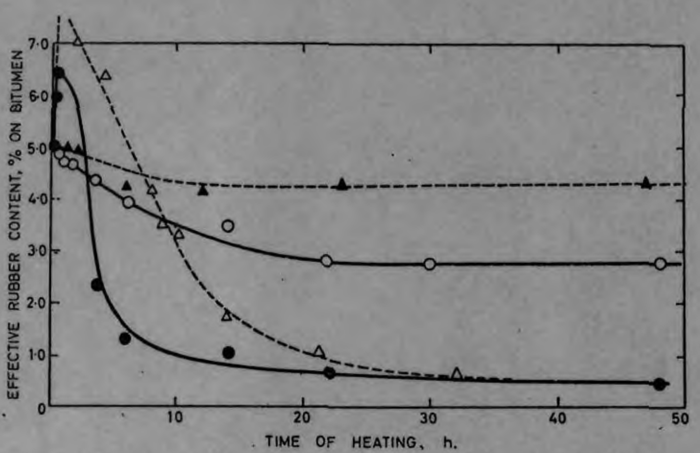

Fig. 3. *Effect of heating on total and effective rubber content of rubber–bitumen*

Material used 5% rubber (latex) in 50 pen. bitumen, 17% kerosene added

— heating at 180° --- heating at 160°

● △ effective rubber ○ ▲ total acetone-insoluble rubber

Note: Effective rubber measured by specific viscosity in benzene, which is function of average mol. wt.

Total rubber is calculated from iodine value and shows the acetone-insoluble rubber regardless of its condition

Table I gives results of the analyses of some rubberised binders used in full-scale road experiments: these show how widely the effective rubber content may differ in comparable materials. These figures show that the results of full-scale experiments and trials with rubberised binders must be interpreted with great care, since the effective rubber content of the binders may be much less than was intended, due to overheating. In some instances the effective rubber content is negligible.

Table I

Some results of the determination of the rubber content of rubber–bitumen

Source of bitumen	Percentage of rubber added (w/w)	Total rubber	Effective rubber
		% by wt.	
Laboratory-prepared rubber–bitumens			
40/50 pen. (Kuwait)	4·35	4·34	4·50
90/110 pen. (Kuwait)	2·60	2·46	2·50
290/310 pen. (Venezuela)	5·65	5·72	5·41
Commercial rubber–bitumens			
Sample A	2·0	1·82	0·44
Sample B	2·0	1·61	0·53
Sample C	50·0	3·43	0·0
Rubber–bitumen recovered from road materials			
Sample D	3·85	2·98	0·27
Sample E	10·5	12·1	3·44
Sample F	12·5	6·67	0·89

Samples C and F show not only complete loss of effective rubber (as measured by the specific viscosity) but also a considerable reduction in the total rubber (as given by the iodine value). This indicates severe degradation; when the polymer is broken down into sufficiently small fragments, it becomes soluble in acetone and is not detected by the methods described.

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ULTRA-VIOLET SPECTROSCOPIC DETERMINATION OF PHENOLIC ANTIOXIDANTS IN STABILISED LANOLIN

By S. LEE and N. A. PUTTNAM

An ultra-violet spectroscopic method is described for the determination of the antioxidant Topanol OC (2,6-di-t-butyl-4-methylphenol) in stabilised Lanolin. The determination is based on the corrected absorbance at 283·5 mμ and the interfering absorptions arising from the Lanolin are removed by compensation with a standard Lanolin solution.

Introduction

2,6-Disubstituted phenols have found extensive use as antioxidants in a variety of products. Wadelin[1] has described the estimation of the antioxidant Wingstay S (2,6-di-t-butyl-4-methylphenol) incorporated into rubbers. Because of the interfering effects of extraneous absorptions arising from the rubbers themselves in the region where these phenols show a characteristic absorption,[2] Wadelin utilised the fact that in alkaline solutions the absorption maxima of these phenols was shifted 20 mμ towards longer wavelengths. This shift arose from the formation of the phenoxide ion.[3] At these wavelengths the interfering absorptions of the rubbers themselves were negligible. The antioxidant was determined from the difference in the absorption at 301 mμ of the sample in neutral and alkaline solution.

Commercial lanolin has also been stabilised with the antioxidant Topanol OC* (2,6-di-t-butyl-4-methylphenol), which is identical with Wingstay S. Lanolin showed a steadily decreasing absorption over the range 247mμ to 312 mμ and hence would interfere with the precise determination of Topanol OC at 283·5 mμ in samples of Lanolin stabilised with this antioxidant. However, it was found that the background absorption, due to the Lanolin, could be removed by compensation with a solution of unstabilised Lanolin and the Topanol OC determined from the corrected absorbance at 283·5 mμ. This procedure is preferred to that of Wadelin since, as Topanol OC is a 'hindered phenol',[4] complete ionisation to the phenoxide ion will only occur at relatively strong concentrations of alkali.[3]

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* Registered Trade Name of Imperial Chemical Industries Ltd.