ANALYSES OF VULCANISED RUBBER GOODS.

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(*Read at the Meeting, December 1, 1909.*)

ALTHOUGH analyses of vulcanised rubber goods, especially rubber tyres, have been published from time to time by ourselves ("Examination of Rubber Tyres," *Chem. News*, 1907) and others, and duplicate analyses are sometimes given, we have not come across any published paper in which the actual proportions of the ingredients used in the manufacture of the goods are given as a check on the analyses. This is no doubt due to the disinclination of manufacturers to divulge the proportion of rubber and other ingredients in their goods.

The results of such parallel tests would be of great value as an aid to the interpretation of the analytical figures, and we therefore decided to make up a series of vulcanised samples and submit them to analysis. This we were in a position to do, having steam-heated mixing rolls and other plant necessary for this type of work.

Five samples of vulcanised rubber were analysed. Nos. 1 to 3 contained mineral matter; of these No. 1 was of the simplest possible composition, consisting merely of mineral matter, sulphur, and rubber, and without any of the numerous organic substances, such as oils, waxes, substitutes, etc., employed in the manufacture of commercial rubber goods. Nos. 2 and 3 are of more complex composition, and the latter contains carbon in a finely divided form. This is frequently added to rubber mixings in the form of lampblack, carbon black, graphite, etc., and is difficult to estimate with accuracy. Nos. 1 and 2 contained litharge in quantity, while No. 3 contained no litharge. Samples Nos. 4 and 5 were of the same composition—viz., 100 parts rubber and 5 parts sulphur. Sample No. 4 was suitably cured and analysed a fortnight later, while No. 5 was overcured and had been kept a twelvemonth,

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during which time it had considerably deteriorated and had become soft and weak. These last two analyses were made with a view to determining the effect of vulcanisation on the acetone and alcoholic potash extracts, and to ascertain how far the mineral and other ingredients were accountable for the high figures for these extracts contained in the analyses of samples 1 to 3.

ACTUAL INGREDIENTS AND PERCENTAGE PROPORTIONS TAKEN FOR THE FIVE
SAMPLES OF VULCANISED RUBBERS ANALYSED.

	No. 1.	No. 2.	No. 3.	Nos. 4 and 5.
Mineral matter (dry)	43·75	57·20	35·0	—
Sulphur	11·25	7·85	4·0	4·75
India-rubber (washed and dried) ...	45·00	28·50	35·0	95·25
Paraffin wax	—	4·30	—	—
Fatty oil	—	2·15	4·0	—
Carbonaceous matter	—	—	22·0	—

The mineral matter consisted of a mixture of minerals commonly employed in rubber mixings. The sulphur was refined flowers practically free from ash, and the rubber was dried washed plantation rubber of para grade.

Before giving the figures obtained on analysis of the vulcanised samples, it will be as well to consider how each ingredient will appear in the analysis. Thus, taking sample No. 1, the mineral matter will be estimated as ash. The figure obtained on analysis may be lower owing to loss of CO_2 from carbonates, or higher owing to retention of sulphur as sulphides, and any mineral matter originally present in sulphur and rubber.

Part of the sulphur will be estimated as free sulphur in the acetone extract, and the percentage of sulphur is deducted from the latter to get the percentage of resinous matter and other constituents of the acetone extract.

The rubber will be estimated by difference. The figures obtained will be smaller, as the rubber contains ash amounting to 0·5 per cent., resins (acetone extract) 3·6 per cent., nitrogenous matter (protein) 2·9 per cent., and caoutchouc 93 per cent. The 45 parts of washed dried rubber are, therefore, composed of—Rubber (caoutchouc), 41·85; resins (acetone extract), 1·6; protein, 1·3; mineral matter (ash), 0·25.

Hence on analysis we should expect to find for sample No. 1:—

Ash (mineral matter as modified by ignition with sulphur *plus* ash of rubber)
= $43·75 + 0·25 = 44$ per cent.

Acetone extract (acetone extract of the caoutchouc as modified by chemical changes during vulcanisation),* = 1·6 per cent.

Alcoholic potash extract (the only constituent likely to be attacked by alcoholic potash is the nitrogenous or protein matter; the amount is small, and we may assume that the whole is decomposed) = 1·3 per cent. This would represent the maximum, and the actual figure might be expected to be lower.

* See analyses of rubber vulcanised with sulphur only, Nos. 4 and 5.

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Caoutchouc (by difference—that is, by subtracting the sum of the above figures and total sulphur from 100. This figure should represent the actual caoutchouc in the dry, washed rubber used) = 41·85.

Similar remarks apply to the other four samples; we need only mention that the paraffin wax will be found in the acetone extract. The same applies mainly to the fatty oil, although that portion which reacts with sulphur becomes insoluble in acetone, but dissolves in alcoholic potash. This latter portion is probably small, and in the tables it is assumed that the whole of the oil is soluble in acetone.

The carbonaceous matter in No. 3 yielded on ignition 29·5 per cent. ash, so that, of the 22 parts, 6·5 parts represent mineral matter, and the remainder, 15·5 parts, organic matter.

In the tables are given for each sample the figures we should expect to obtain on analysis as calculated from the proportions of ingredients taken, and, alongside, the actual figures obtained on analysis.

	1.		2.		3.		4 & 5.	4.	5.
	Calculated.	By Analysis.	Calculated.	By Analysis.	Calculated.	By Analysis.	Calculated.	By Analysis.	By Analysis.
Mineral matter or ash	44·0	44·75	57·3	58·3	41·7	41·0	0·5	0·5	0·6
Acetone extract (resins, waxes, oils, etc.) ...	1·6	2·7*	7·45	5·0*	5·25	5·8*	3·4	5·0	20·3
Alcoholic potash extract (substitutes, protein, etc.)	1·3	5·65	0·8	10·4	1·0	2·7	2·65	0·9	6·35
Carbonaceous matter	—	—	—	—	15·5	15·1	—	—	—
India-rubber or caoutchouc (by difference) ...	41·85	35·65	26·60	18·45	32·55	31·40	88·70	88·85	68·00

In carrying out the above analyses, we were prepared to find differences between the calculated figures and those obtained on analysis, but we were not prepared to find the large differences we observed.

All the samples examined were good specimens of commercial qualities with the exception of No. 5, which was analysed to see what effect would be produced on the analysis by over-vulcanising and keeping.

A comparison of the analytical results of Nos. 4 and 5 gives us a clue to some of the anomalies observed. It is well known that after vulcanisation rubber shows a

* Acetone extract as ordinarily determined less the free sulphur contained in it.

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higher acetone extract than in the raw unvulcanised state. Weber (*J. Soc. Chem. Ind.*, 1894, 13, 3650) has observed this, and states that vulcanised para yields 3 to 4·5 per cent. extract, but he has not called attention to the equally striking increase in the alcoholic potash extract. To realise these figures, they require to be calculated on the rubber (caoutchouc), and we give them below in this form, and also the total percentage, as calculated, of all matter which could possibly be extracted by acetone and alcoholic potash.

PERCENTAGE EXTRACTS CALCULATED ON WASHED, DRIED RUBBER ONLY.

	1.	2.	3.	4.	5.
Acetone extract	6·0	17·5	16·6	5·2	21·3
Alcoholic potash extract	12·6	36·4	7·7	0·9	6·7
The sum of both extracts	18·6	53·9	24·3	6·1	28·0
Total amount of substances in mixing capable of extraction by these reagents, and calculated on the rubber	6·4	12·9	10·4	6·4	6·4
Percentage of rubber converted to soluble product (resin?)	12·2	41·0	13·9	—	21·6

We have included in the total amount of substances possible of extraction with acetone and alcoholic potash every organic constituent of the rubber mixing, including the resin and protein matter in the rubber itself. It is very doubtful whether the latter is even partially removed by this treatment, and consequently the last row of figures may be a little too low, but are certainly not too high. It will be seen that the quantity of extractive matter varies enormously with the same rubber when compounded with different ingredients, and that this may amount to not less than 41 per cent. in a sample of properly cured rubber.*

It would be premature at this stage to put forward any theory on the experimental figures here given, but a careful study of this aspect of vulcanisation with analyses of graded mixings should throw much light on the deterioration of rubber goods on keeping. Needless to say that, with such irregular figures for these extracts, the results of caoutchouc determinations by difference can only mislead, and, as will be seen from the tables, are almost invariably too low.

The only figures which at all approximate to actual values are those for mineral matter determined as ash. In the three samples the figures found on analysis vary from 1 per cent. too high to 0·7 per cent. too low, an approximation certainly as close as one could expect, considering the possibility of errors in either direction, as already indicated.

It is obvious, from the foregoing, that the greatest care is necessary in the interpretation of the figures obtained on analysis of vulcanised rubber goods. In no case is the chemist justified in regarding the alcoholic potash extract as a measure

* We have samples of these rubbers a twelvemonth or more old in perfect condition, which were vulcanised at exactly the same time and temperature as the samples analysed.

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of substitutes added. This figure is frequently 5, and may easily reach 10 in vulcanised samples in the manufacture of which no substitute has been used. We speak from experience of other samples besides those quoted above. It is also apparent that the percentage of rubber as determined by difference may be entirely misleading, and is usually lower than that actually added. The age and condition of the goods will also affect the analytical results, and must be taken into consideration.

In general, the results of analyses yield valuable information in the examination of rubber goods when all circumstances are taken into consideration, and especially in conjunction with physical tests; but without some knowledge of manufacturing conditions and the requirements of users the analytical results are not only worthless, but may be misleading.

DISCUSSION.

Dr. P. SCHIDROWITZ congratulated the authors on the closeness with which their figures obtained by difference for the proportions of caoutchouc agreed with the calculated proportions, especially having regard to the figures obtained by saponification. It would be interesting to know of what the saponifiable matter consisted. He agreed that it might be quite wrong to return any difference in weight after saponification as rubber substitute. It was merely saponifiable matter. On the other hand, if it was not there in the first instance, it must obviously have been formed in the process either of mixing or of vulcanisation, and it was therefore not normal rubber and could not properly be returned as such. In such cases the goods had simply been mixed and vulcanised in such a way as to destroy some of the rubber or convert it into matter soluble in alcoholic potash. It was possible to estimate directly the proportion of caoutchouc by dissolving the rubber substance with a solvent of high boiling-point and estimating the caoutchouc as a bromide. Although the results tended to be a little too low, especially in the case of high-class mixings, he had found this method (Axelrod), as a rule, to answer well. With very complex mixtures the results were not so good, but calculating from the bromide and adding 10 per cent., it appeared that a very close approximation was obtained. He had analysed in this way a number of samples of which he knew the composition, and had obtained satisfactory results. In the case, for instance, of one sample containing about 90 per cent. of rubber, the bromide method showed 85 per cent. The process, moreover, had the advantage of speediness, whereas the difference method took a somewhat long time. The mineral matter, too, could be generally directly determined by the Axelrod method, provided that free carbon was not present.

Mr. J. GOLDING, referring to the authors' remark as to the difficulty of separating the carbonaceous matter, said that he had recently obtained a centrifugal apparatus for bacteriological work which he had found very useful for separating substances difficult to filter. It was capable of dealing with a bulk of 360 c.c. at one time, and worked at 4,000 revolutions per minute.

Dr. H. P. STEVENS said that they had tried a centrifugal apparatus of the ordinary type for separating the carbonaceous matter, but without success. They had not

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tried the bromide method referred to by Dr. Schidrowitz, but several other methods which they had tried for the direct estimation of the caoutchouc had proved unsatisfactory. In the case of high-class rubber goods the difference method seemed to give a closer approximation than the bromide method, judging the latter by the figures mentioned by Dr. Schidrowitz; while with goods containing a smaller proportion of caoutchouc the approximation obtained by the difference method would probably be still closer. Thus it would be seen that in the case of sample No. 4 the difference method showed 88·85 per cent., as against the calculated percentage of 88·7, whereas Dr. Schidrowitz by the bromide method obtained 85 per cent. in place of 90 per cent.

Dr. P. SCHIDROWITZ said that he had obtained satisfactory results by the bromide method with samples containing as little as 30 to 35 per cent. of caoutchouc.

Dr. H. P. STEVENS said that the nature of the mineral matter used would probably make a considerable difference. If the bromide method gave higher results than the difference method, it would mean that products were included and reckoned as caoutchouc which were not actually rubber, but decomposition products of rubber. The results obtained by extraction with alcoholic potash seemed to show conclusively that in the process of vulcanisation the rubber was broken down, though the nature of the resulting products was not at present known.

Mr. O. HEHNER asked how the amount of extract in the alcoholic potash solution was determined. If it was determined merely by difference, it seemed likely that, if litharge or zinc oxide were used in the mixture, some proportion of these might be dissolved. He suggested that it would be better to precipitate the organic matters by the addition of hydrochloric acid.

Dr. H. P. STEVENS agreed. In making these analyses, however, they had followed the ordinary recognised process.