

## RECENT ADVANCES IN THE ANALYSIS AND EVALUATION OF RUBBER AND RUBBER GOODS.\*

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### I. CRUDE RUBBER.

THE examination of crude rubber may involve :

- (a) *Chemical Analysis*, with a view to determining the quantity of pure rubber and of various "impurities," and, to a certain extent in some instances, the nature of the latter.
- (b) *Physical or Mechanical Tests*, carried out either on the crude material or on the latter modified by the vulcanisation process, with a view to determining the physical or mechanical qualities of the rubber substance.

Hitherto *chemical analysis* has played a somewhat subordinate part in the commercial evaluation of crude rubber, partly on account of our lack of exact knowledge regarding the nature of the secondary products (resins, nitrogenous substances, etc.), partly owing to the absence of specific information on the influence exercised by them on the vulcanisation process on the one hand, and on the more important attributes (strength, elasticity, etc.) on the other hand. If the difficulties associated with the chemical investigation of the nature and influence of the "impurities" necessarily make progress in this direction slow, it is not surprising that work having as its object the identification and evaluation by chemical means of different rubber substances or caoutchoucs, is still in a more or less embryonic state. In this connection, however, may be mentioned the work of Gottlob (*Gummi-Zeit.*, 1907, **22**, 305; of Harries, *Annalen*, *loc. cit.*, *infra*) on the fission products of caoutchouc ozonides obtained from rubber of different sources, and of Harries on the rate of decomposition of these substances (*Annalen*, 1913, **395**, 211; *Zeitsch. angew. Chem.*, 1912, **25**, 1457; *Ber.*, 1908, **41**, 3552). Some comparatively recent work by Caspari (*J. Soc. Chem. Ind.*, 1913, **32**, 1041) suggests the possibility of discriminating, up to a point, by physico-chemical methods, between caoutchoucs of different commercial quality. According to Caspari, rubber is of a composite character, and consists (1) of "soluble" rubber—a weak but elastic colloid, soluble in light petroleum—and (2) of "insoluble" or "pectous" rubber—an elastic colloid of considerable mechanical strength. The latter, which in some respects resembles a slightly vulcanised material, preserves its structure on contact with solvents. It is, however, gradually dissolved by benzene and carbon tetrachloride, but whereas, for instance, the viscosities of the "soluble" in Brazilian and Plantation Para respectively are very similar, the "pectous" in the latter is far more readily attacked by benzene or carbon-tetrachloride than the "pectous" of the former. According to Caspari, fine Brazilian

\* This is the second of a series of articles dealing with recent advances in certain branches of analytical work. Others will follow at intervals.—EDITOR.

grades contain 35 per cent. to 80 per cent. of pectous, whereas plantation rubbers examined by him showed no more than 10 per cent. to 25 per cent. Caspari appears to believe that "nerve" or strength is mainly due to the "pectous" variety. While the work of Caspari will require confirmation and much amplification before it can be applied to practical rubber evaluation, the writer has referred to it at some length, inasmuch as it suggests a new field of research, and one which at least indicates the possibility of estimating *quality* by a direct physico-chemical method.

*Investigations on Secondary Products*—(a) *Rubber Resins*.—Hinrichsen and Marcusson (*Zeitsch. angew. Chem.*, 1910, **23**, 49; *ibid.*, 1911, **24**, 725) have examined the resins from a number of commercial grades in regard to optical activity, saponification, and iodine absorption values. The outstanding feature in this work is that all resins, excepting that from Para (*Hevea*), are optically active. In certain cases, therefore, the absence of optical activity in the extracted resin may be taken as evidence that no rubber other than *Hevea* is present. Para resin contains roughly 15 per cent., other rubber resins up to 100 per cent., of unsaponifiable matter. The optical activity appears to be mainly due to the latter. Iodine values varying from 30.6 (Hübl) for Jelutong resin to 118 for Para resin were found. So far as the investigation has been carried, it appears that the resins from vulcanised rubber exhibit the same characteristics as those extracted from the crude material. D. Bloom (*Chem. Zeit.*, 1912, **36**, 815), as the result of the examination of about 150 samples of resin from different species, came to the conclusion that the "acid value" of the resin from the same species is a constant. M. Klassert (*Zeitsch. angew. Chem.*, 1913, **26**, 471; *ANALYST*, 1913, **38**, 465) examined the resins obtained from a number of species, and found melting-points 110 to 119° C. (not sharp); ash, 0.8 to 2.5 per cent.; iodine value (Hübl), 28.3 to 36.3; saponification value, 62.3 to 90.5; acid value, 0.9 to 1.2; ester value, 61.4 to 89.2. Hinrichsen (*ANALYST*, 1913, **38**, 336) recommends that the extraction of resin should be carried out in an apparatus of brown glass, to avoid the effect of light. The effect of rubber resin on *vulcanising capacity* has been the subject of some controversy. Lothar E. Weber (*Eighth Int. Congress Appl. Chem.*, 1912; *J. Soc. Chem. Ind.*, 1912, **31**, 888), using a mixture containing *inter alia* litharge, concluded that the extraction of resin renders the rubber practically incurable; D. Porritt ("Chemistry of Rubber," London, Gurney and Jackson, p. 46) finds that the absence of resin renders litharge almost inoperative as a catalyst. On the other hand, Beadle and Stevens (*India Rubber J.*, 1913, **45**, 313; also *Koll. Zeitsch.*, 1914, **14**, 91; *ibid.*, 1913, **12**, 46; *ibid.*, 1912, **11**, 61) did not find that resin exercised any marked effect on curing capacity, but these workers employed a mixture containing no litharge or other catalyst.

"*Insoluble*" Matter: *Nitrogenous Substances*.—In a general way the term "insoluble matter" is not applied to accidental mechanical impurities (such as sand, bark, soil, etc.), but to the natural and normal substances always present to some extent in crude rubbers. *Mechanical Impurities*.—Beadle and Stevens (*ANALYST*, 1912, **37**, 13) have devised a method aiming at the determination of mechanical impurities only. This consists, substantially, in "depolymerising" the rubber by heating with a solvent of high boiling-point, thinning still further with a solvent of low viscosity, filtering, and weighing. Under these conditions it is claimed that the

"insoluble" (protein, etc.) is broken up, the mechanical impurities alone remaining. *Nitrogenous Substances*.—While there is no rigid proof that normal "insoluble" is essentially a nitrogen product (a part of the same frequently, without serious doubt, consists of oxidation products), it is now fairly certain that it normally contains a high proportion of nitrogen. There is some controversy as to the general nature of the nitrogen-bearing substance. Spence (*J. Inst. Commercial Research in Tropics*, No. 13; *J. Soc. Chem. Ind.*, 1907, **26**, 1287), to whom we are indebted for the discovery of the nitrogenous character of the "insoluble," in the course of earlier work (*loc. cit.*) found that it contained at the most 5·4 per cent. of nitrogen, and came to the conclusion that it was probably a glyco-protein. Subsequently, A. Tschirch and W. Schmitz (*Gummi-Zeit.*, 1912, **26**, 2079; *ANALYST*, 1913, **38**, 272), and the latter in a further paper (*Gummi-Zeit.*, 1913, **27**, 1085), found that by the method of separation referred to below, a product could be obtained containing from 14 to 16 per cent. of nitrogen—*i.e.*, a figure agreeing with that found in simple proteins. The authors mentioned admit, however, that the qualitative reactions are not those characteristic of proteins. Spence (*Koll. Zeitsch.*, 1914, **14**, 262), also adopting a new method of separation (*cf.* below), obtained a product containing at most 10 per cent. of nitrogen, and showing reactions characteristic of the glyco-proteins. Spence argues that Schmitz' results are unreliable, as the latter based his statements regarding nitrogen-content on the results of analyses made by the Kjeldahl method; but as Schmitz' results were *higher* than those of Spence, the latter's argument is not very illuminating. *Methods of Separation and Estimation*.—W. Schmitz (*loc. cit.*) found that by treating 2·5 grms. of rubber with 50 c.c. of pentachlorethane for five to seven hours at 85° to 90° C., a very fluid solution, readily filterable, particularly if somewhat diluted with chloroform, could be obtained. The residue may be further purified by dissolving in 5 per cent. sodium hydroxide and reprecipitating with hydrochloric acid. D. Spence and G. D. Kratz (*loc. cit., supra*) found that if crude rubber is heated with a solvent such as benzene, and a small quantity of a strong acid is added, the "depolymerising" effect\* of the latter is so great that, for example, the liquid obtained by the action of 0·3 to 0·5 per cent. of trichloroacetic acid on 100 grms. of rubber suspended in 1 litre of benzene (after standing for forty-eight hours in sunlight) may be separated from the bulk of the insoluble matter by simple decantation. The "insoluble" may be further purified by repeated treatment with acidified solvent, and finally with pure solvent. Spence considers that the "depolymerising" effect of the solvent used by Schmitz (pentachlorethane) is really due to the hydrochloric acid split off from the latter. G. Bernstein (*Koll. Zeitsch.*, 1914, **15**, 49) states that the viscosity of rubber solutions may be readily reduced to approximately that of the solvent by the action of ultra-violet rays generated in a quartz-lamp.

*Practical Considerations*.—There is considerable evidence to warrant the assumption that the "insoluble" matter in crude rubber has an important bearing on vulcanising capacity, but hitherto no quantitative relationship has been discovered.

\* D. Spence (*Koll. Zeitsch.*, 1909, **4**, 70) had previously noted the remarkable reduction in viscosity produced in rubber solutions by traces of a mineral acid.

While, on the one hand, Beadle and Stevens' work (*loc. cit.*) shows that the removal of "insoluble" markedly decreases curing capacity, the writer's practical experience so far is that rubbers with a low proportion of "insoluble" do not necessarily cure badly, nor, conversely, do samples containing a high proportion necessarily vulcanise rapidly. It is highly probable that the "insoluble" varies considerably in composition,\* and, if this is so, further methods of separation will have to be devised before the "insoluble" can be taken as a criterion of quality. While Spence's and Schmitz' (*loc. cit.*) methods of separation are obviously convenient, it will be desirable, before adopting them for analytical or research purposes, to obtain satisfactory evidence that the strong acids employed are without action on the insoluble substances.† Meanwhile the writer prefers for analytical purposes the indirect method (Schidrowitz, "Rubber" [Methuen], p. 252), which consists in evaporating a convenient volume of clear solution—obtained by treating 0.5 to 1 grm. of rubber with 100 to 200 c.c. of benzene in a tall cylinder, whirling gently at intervals, and then allowing to settle—pipetted from above the settled "insoluble" and weighing the residue.

*Estimation of Rubber.*—The fundamental difficulty of differentiating with certainty between soluble and "insoluble" matter, not to speak of the cognate problem of accurate separation, has an important bearing on the estimation of caoutchouc in the raw material. This applies to the indirect or difference methods as well as to the direct methods (determination as bromide, nitrosite, or nitrosate). With regard to the former set of methods this is obvious; with regard to the latter, it may be indicated that separation is either an essential preliminary, or, if not, the "insoluble" matters are likely to form halogen or nitrosite compounds on their own account. Fortunately, the problem, regarded from a purely technical or practical point of view, is not of any great moment. The great bulk of the rubber now coming to market (plantation rubber and fine Brazilian grades) shows very little variation for the same commercial grades in regard to resin, ash, and nitrogen content respectively. Within reasonable limits, therefore, the figures for resin, ash, and nitrogen are of very little value as a criterion of commercial quality. Assuming a satisfactory method of separating the "insoluble" matter, the most satisfactory indirect method of estimating caoutchouc or rubber is by deducting the sum of moisture + resin + insoluble matter from 100. This method involves the assumption that the whole of the ash and nitrogen are present in an insoluble form. At the present time the writer considers that the most suitable way of returning the results of a technical crude rubber analysis is as follows :

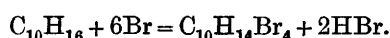
\* Beadle and Stevens (*India-Rubber J.*, 1913, **45**, 313) show that there is no apparent connection between the amount of "insoluble" and the nitrogen content in a rubber.

† A recent paper by J. G. Fol (*International Rubber Congress, Batavia*, 1914, published by J. H. de Bussey, Amsterdam, p. 446) clearly indicates the importance of adopting a standard method of some kind for the determination of "insoluble." Shaking, heating, previous mechanical working, and other influences, have an enormous influence on the quantitative results obtained (extreme variations for the same sample, 0.65 per cent. – 20.0 per cent.). Similar observations have been made by Beadle and Stevens and by Caspari. The explanation of these apparently anomalous results is, no doubt, that shaking, maceration, etc., break up a part of the "insoluble" matter, and, conversely, of the rubber proper, into very fine particles, which are either so transparent or so fine as not to be noticeable.

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	Per Cent.			
Moisture	...	...	...	—
Resin (acetone extract)	...	...	...	—
Insoluble matter	...	...	...	—
Rubber (by difference)	...	...	...	—
<i>The above contains—</i>				
Ash (mineral matter)	...	...	...	—
Nitrogen	...	...	...	—
„ = protein	...	...	...	—

These notes, it must be understood, apply only to routine technical analysis, of which the chief object is to ascertain—mainly from the point of view of controlling methods of production or of gauging suitability for specific manufacturing purposes—whether or not any distinct abnormality is disclosed. For research purposes the direct methods should be kept in view. In this respect the original work of Budde, Harries, and Alexander respectively, on bromination and nitrosation methods may be supplemented by the following brief references to papers of recent date: W. Vaubel (*Gummi-Zeit.*, 1912, **26**, 1879) employs a bromination method which consists in treating a solution of rubber in carbon-tetrachloride with potassium bromate, and titrating the excess of the latter in the usual way. The reaction is stated to be—



F. Kirchof (*ibid.*, 1912, **27**, 9) was unable to confirm Vaubel's results. According to the former, the amount of HBr split off largely depends on the purity of the reagents, temperature, and concentration. The presence of hydrobromic acid is due to decomposition of the *tetrabromide*. Returning to the attack, Vaubel (*ibid.*, 1913, **28**, 92) in a joint paper with E. Weinerth states that his method gives results concordant with those obtained with the bromination processes of Budde and Axelrod, but admits that it requires further development before it can be regarded as generally applicable. K. Utz (*ibid.*, 1912, **26**, 968), in a review of the bromide methods, suggests that a French process, in which the tetrabromide is oxidised with chromic acid mixture, possesses advantages. Pontio (*Ann. Chim. analyt.*, 1914, **19**, 60; *ANALYST*, 1914, **39**, 179) condemns all methods depending on the use of a solvent of low boiling-point. He prefers the indirect method, but of the direct methods described he regards Budde's tetrabromide process as the most promising.

*Estimation of Moisture.*—A recent paper by J. G. Fol (*loc. cit.*, 439) confirms the practical experience of the writer, which is to the effect that drying in the air-oven at 100° C. does not involve any serious error owing to oxidation. An examination of six samples showed that the results obtained at 100° C. in air and in a stream of carbonic acid respectively are substantially the same. Drying over sulphuric acid in a vacuum at room temperature gave *lower* results than drying either in air or in carbonic acid. These results and further direct experiments lead Fol to the conclusion that the effect of oxidation during a two hours' heating in the air-oven may be neglected. In the opinion of the writer, moisture is best determined (1) by drying in the water-oven at approximately 98° C. until an *increase* of weight becomes apparent, or for a standard time of two hours; or (2) by taking the difference



between the original weight of the sample and the weight after the acetone extraction plus the extract. *Washing Loss*.—It is generally agreed that if the sample is sufficiently large, and if it requires washing, that the analytical determinations generally should be carried out on the washed, air-dry material.

*Physical and Mechanical Tests—Viscosity*.—The work of Axelrod (*Gummi-Zeit.*, 1905, **19**, 1053; *ibid.*, **20**, 105) and of Schidrowitz and Goldsbrough (*J. Soc. Chem. Ind.*, 1909, **28**, 3; "The Rubber Industry," 1911, 260) indicated that the determination of viscosity was likely to afford a valuable criterion as to quality; or that, at least, it would prove of practical utility as a "sorting out" test where vulcanisation tests could not be applied. Further experience of the writer and others suggests that while a decidedly low viscosity figure is almost invariably a sign of poor quality, the converse does not always hold good. This may be due (*cf.* Caspari, *loc. cit.*) to the difficulty of satisfactorily separating suspended (minute or transparent) particles. In view of the relationship between viscosity, swelling capacity, and solvate formation (E. Hatschek, *Koll. Zeitsch.*, 1913, **12**, 213; E. Posnyak, *Koll. Chem. Beiheft.*, 1912, **3**, 417; F. Kirchof, *Koll. Zeitsch.*, 1914, **15**, 30) it seems possible that a determination of imbibition or swelling capacity (*cf.* Caspari, *loc. cit.*) may give more satisfactory results. J. Fol (*Koll. Zeitsch.*, 1913, **12**, 131) suggests that the viscosity curve should be calculated in terms of the subtended area, and that this method is preferable to the tangent method of Schidrowitz and Goldsbrough (*loc. cit.*). R. Gaunt (*J. Soc. Chem. Ind.*, 1914, **33**, 446) finds that by plotting the logarithms of the viscosity (efflux time) numbers against concentration, a straight line is obtained, and advocates that the inclination of this line to the *abscissa* shall be taken as a measure of viscosity. *Adhesion Tests*.—Clayton Beadle and Stevens ("The Rubber Industry," 1911, 274) determine the load required to separate pieces of paper evenly coated with a solution of the rubber. The paper is coated by drawing it over the surface of the (5 per cent. or less) solution. *Mechanical Tests*.—The writer is of opinion, as the result of published (*cf.* *India-Rubber J.*, 1912, **44**, 1147, 1198) and unpublished work, that mechanical (tensile) tests carried out on raw (unvulcanised) rubber are of no practical value. Considering that manufacturers and experts generally appear to agree that, regarded as *criteria* of quality, appearance (colour, etc.), and strength of crude rubber are of very little value, it is remarkable that the bulk of the rubber produced is still sold on rule-of-thumb, "sight-and-pull" tests.

*Vulcanisation Tests*.—With insignificant exceptions rubber is employed in the arts and commerce in the vulcanised state. In the process known as *hot curing*,\* which is used for the bulk of the goods (tyres, hose, buffers, valves, shoes, etc.) manufactured, the following factors, so far as we are aware, have an influence either on the course of the process or on the quality or durability of the wares: (a) *Material*.—State of aggregation (degree of "polymerisation") or physical condition of the rubber substance; quantity and nature of resin and of "insoluble" matter; acidity (?). (b) *Process*.—Temperature, duration of heating; method of heating; quantity of sulphur; if fillers are used, the nature and quantity thereof. So long as our knowledge of the physical and chemical nature of the impurities and

\* This consists, substantially, of the interaction of masticated rubber (with or without fillers, pigments, etc.) with elementary sulphur at a temperature above 130° C.

of the rubber substance in crude rubber is incomplete, it is naturally impossible to devise any method of analysis or physical tests which will enable us to determine, quantitatively, the effect of the various factors on vulcanisation. Direct vulcanisation tests are therefore, for the present, essential for the purpose of practical evaluation. Very broadly it may be stated that such tests may comprise (a) observations regarding the behaviour of the material during, or rather towards, the process; (b) observations on the nature of the vulcanised product. With regard to (a) the writer considers the most important point to be *rate of cure* (cf. Schidrowitz, *The Rubber Industry*, Conference Book, Rubber Exhibition, 1914, p. 215). In this connection the writer relies entirely on an examination of the mechanical properties of the vulcanisate; there appears to be no direct connection between the "coefficient of vulcanisation" (i.e., combined sulphur) and the technical properties of the material (author's unpublished work. Cf. also Spence, *Koll. Zeitsch.*, 1912, **10**, 299; *ibid.*, 1912, **11**, 274; *ibid.*, 1913, **13**, 41 and 265). Various types of tests have been proposed and are applied to vulcanised rubber—namely, *tensile tests* (Schidrowitz, *Rubber* [London, Methuen, 1911]; also *Rubber Industry*, 1914, *loc. cit.*; J. Fol., *Batavia Congress*, 1914, 456; Clayton Beadle and Stevens, *Rubber Industry*, 1911, 265; Memmler and Schob, *Arbeit. des. Kgl. Materialprüfungsamt*, 1909, **4**. Also Memmler, *Rubber Industry*, 1911, 351; Stratton, *Bureau of Standards*, U.S.A. *Circular*, **38**, 1912, such as breaking-strain, elongation, stress, strain, curves to the break); *hysteresis tests* (Schwartz, *J. Inst. Elect. Engin.*, 1910, 701; Shedd and Ingersoll, *Phys. Review*, 1904, **19** [2], 107; Clayton Beadle and Stevens, *loc. cit., sup.*, and *India-Rubber J.*, 1912, **44**, 603; 1913, **46**, 161); *elasticity tests* (P. Breuil, *Le Caout. et la Gutta.*, 1908; Memmler, *loc. cit.*, 365); *hardness tests* (Breuil, *loc. cit.*; Memmler, *loc. cit.*); *abrasion tests* (Memmler, *loc. cit.*; *ibid.*, *Gummi-Zeit.*, 1912, **27**, 2; Clayton Beadle and Stevens, *ibid.*, 1912, **27**, 167; Schidrowitz, *loc. cit.*), etc., but it is necessary to bear clearly in mind the essential difference between tests designed for the comparative evaluation of crude rubber and tests applied with a view to examining the specific properties of any given (vulcanised) rubber article. With regard to the former it is desirable to use methods calculated to measure certain intrinsic and typical properties of the raw material, such as curing capacity, strength, distensibility, capacity for recovery (Schidrowitz, *Batavia Congress*, 1914, 371; *ibid.*, *Rubber Industry*, 1914; also Standardisation Report, *India-Rubber J.*, 1913, **46**, 1215). In view of the factors which are of influence on the vulcanisation process, it is obvious that any system of evaluation based thereon must be carried out under strictly standardised conditions of mixing, curing and testing. The writer considers a "pure" rubber and sulphur mixing the most suitable for the purpose, partly for the reason that the introduction of a filler\* renders the reaction less delicate, partly because a "pure" mixing is less likely to be heterogeneous† than one containing minerals.

\* The reference is to *inert* fillers. The use of fillers having a specific action would obviously still more complicate matters.

† Skellon (*Koll. Zeitsch.*, 1904, **14**, 96) has shown that if doughs (i.e., uncured mixes) containing widely different quantities of sulphur are vulcanised in contact with one another, a wandering of the sulphur to an equilibrium throughout the mass takes place. It seems (although no work on the subject has been published) highly improbable that a similar phenomenon would occur in the case of fillers, particularly of such as do not melt at the temperatures employed.

## II. VULCANISED RUBBER.

*Analysis.*

*Preparation for Analysis.*—L. Archbutt (ANALYST, 1913, **38**, 550) recommends, for purposes of comminution, a pair of grooved rollers, working either in gear (3 : 2) or with one roller fixed. The machine has partly a cutting, partly a grinding action, which varies according to the adjustment of the rolls. It is stated that all commercial grades can be readily reduced to a good sample by the machine without further treatment.

*General Scheme of Analysis.*—The Henriquez-Weber scheme (C. O. Weber, "The Chemistry of India-Rubber," London, Griffin, 1902), details of which may be found in every textbook on the subject, is still the basis of quantitative rubber analysis. In one respect, however, it requires serious modification. The work of Britland and Potts (*J. Soc. Chem. Ind.*, 1910, **29**, 1142) and others has shown that pyridine frequently attacks rubber, and this solvent, therefore, can no longer be recommended for the separation and estimation of the pitch, asphalt, and bitumen group of fillers. Caspari ("Technical Methods of Chemical Analysis," Lunge-Keane. London, Gurney and Jackson, 1914, Vol. III., Part I., 426) states that ethyl acetate following acetone sometimes gives good results. R. Becker (*Gummi-Zeit.*, 1911, **25**, 598) recommends carbon bisulphide, and Potts ("The Chemistry of the Rubber Industry," London, Constable, 1912, 132) confirms Becker's view that extraction for one hour in the Zuntz type of apparatus with carbon bisulphide swells but does not appreciably dissolve rubber. It is not clear, however, whether this refers to all types of mixings. The writer prefers to make a preliminary qualitative test with cold benzene or, preferably, nitro-benzene. If the solvent does not become appreciably (yellow to brown) coloured or fluorescent, it may be assumed that no appreciable quantity of bitumen, "mineral-rubber," or similar material has been used. It should be borne in mind, however, that substances of this class vulcanise to a certain extent, and may be modified as regards solubility in consequence. If qualitative tests give a positive indication, the analyst must be guided by the general character of the mixing as to choice of methods. If indirect methods are not available, an extraction with cold nitro-benzene (as originally proposed by Henriquez) or with carbon bisulphide (*cf.* above) may be resorted to.

*Separation of Minerals, Starch, Fibres, etc.*—In Weber's scheme nitro-naphthalene was recommended for this purpose. The writer, in common probably with the majority of other workers on rubber, has abandoned this inconvenient solvent, using as a rule high boiling petroleum (Axelrod, *Gummi-Zeit.*, 1907, **21**, 1229; Hinrichsen, *Chem. Zeit.*, 1909, **33**, 184, and *ibid.*, 735). Frank and Marckwald (*Gummi-Zeit.*, 1908, **22**, 134) recommend xylene under pressure. Anisol at a moderate temperature has also been suggested by Hinrichsen ("Der Kautschuk und seine Prüfung," Leipzig, Hirzel, 1910, 126) and collaborators. F. Jacobsohn (*Gummi-Zeit.*, 1913, **27**, 1906) prefers a mixture of petroleum and camphor oil.

*Estimation of Sulphur.*—D. Spence and J. Young (*J. Ind. and Eng. Chem.*, 1912, **4**, 413; *J. Soc. Chem. Ind.*, 1912, **31**, 651) have devised an electrolytic method



which is stated to give accurate and rapid results; 0.5 grm. material is treated first with nitric acid (sp. gr. 1.4), then with fuming nitric acid. A current of 3 amps. at 8 volts is suitable for the process, which in the case of high-grade soft rubber takes two to three hours as against three-quarters of an hour for low-grade hard rubber. After electrolysis the solution, to which 1 grm. of sodium carbonate is added, is evaporated to dryness, then evaporated with hydrochloric acid, and finally precipitated with barium chloride in the usual way. For soft rubbers the barium chromate volumetric process (*J. Soc. Chem. Ind.*, 1904, **23**, 31) may be used for the final determination, provided the sulphur content is within certain limits. Kaye and Sharp (*India-Rubber J.*, 1912, **44**, 1189) have described a rapid method (two to three hours), which consists in heating 0.25 grm. to 0.5 grm. of the sample with zinc oxide and potassium nitrate. The melt is taken up with hydrochloric acid and precipitated with barium chloride in the usual way. Utz (*Gummi-Zeit.*, 1914, **28**, 631; *ANALYST*, 1914, **39**, 368) finds that this method gives sufficiently accurate results for technical purposes, and suggests some minor modifications. H. P. Stevens (*ANALYST*, 1914, **39**, 74) states that oxidation with nitric acid in an open vessel may lead to serious losses, owing to the formation of volatile sulphur-containing bodies. This may be avoided either by working in a vessel connected with a condenser, or by passing the gases evolved through potash or nitric acid. R. Gaunt (*ANALYST*, 1915, 9) heats the rubber in a stream of oxygen in a combustion tube and collects the sulphur dioxide formed in a solution of hydrogen peroxide. The sulphuric acid formed is determined in the usual way, after boiling with hydrochloric acid to decompose the excess of peroxide. In rubber containing mineral matter the sulphates in the residual ash must also be estimated.

*Estimation of Rubber—Direct Methods.*—It cannot be stated that any of the direct methods can be relied upon to give even approximately correct results in regard to all grades of vulcanised rubber. Nevertheless, in the absence of substances (other than rubber) likely to form nitrosites, bromides, etc., or if the non-rubber nitrous acid or bromine derivative is not capable of interfering or can be allowed for, one or other of the direct methods may frequently be employed as a useful check on or confirmation of the indirect method. It may happen, also, in the case of simple mixings, or of mixings the general nature of which is well known, that a direct method may be of convenience in regard to control or rapidity of work. Alexander's (*Gummi-Zeit.*, 1907, **21**, 653) nitrosite method and Axelrod's (*ibid.*, 1907, **21**, 1229) tetrabromide method have been described in practically every modern textbook, and need not, therefore, be referred to at length. The writer has no experience of the nitrosite method, but it is certainly (*cf.* Potts, *op. cit.*, 141) long and tedious. Axelrod's method has, in the case of soft rubbers, frequently given useful results in the writer's laboratory. Hübner's Method (*Chem. Zeit.*, 1909, **33**, 11; *ANALYST*, 1909, **34**, 170 and 365), although modified by him with a view to preventing loss of bromine (*Gummi-Zeit.*, 1912, **26**, 1711), has been the object of much criticism and suggestion (*cf.* Potts, *op. cit.*, 141; Hinrichsen and Kindscher, *Chem. Zeit.*, 1912, **26**, 217 and 230; Hübner, *Gummi-Zeit.*, 1912, **26**, 1281; R. Becker, *ibid.*, 1503; P. Alexander, *Chem. Zeit.*, 1912, **36**, 554). The impression of the writer is that for certain types of mixings the method and its principles are worth keeping

in mind, and that it might well repay further investigation. C. R. Bogg's (*Int. Congress Appl. Chem.*, 1912; *Koll. Zeitsch.*, 1913, **12**, 86) proposes a modified Axelrod-Budde method in which toluene is used as a solvent and the bromine is finally titrated. In the opinion of the writer toluene is not likely to be effective except in the case of very soft mixings. W. A. Ducca (*ibid.*), who has investigated a number of direct methods, concludes that the nitrosate methods are useless both for crude and vulcanised rubbers; that Budde's method is good for crude but not for vulcanised goods, and that Hübner's method is unreliable. P. Goldberg (*Chem. Zeit.*, 1913, **37**, 85; *ANALYST*, 1913, **38**, 111) distils off the caoutchouc (in a combustion tube) at a temperature not exceeding 400° C. in a current of nitrogen, and weighs the residue. The difference represents vulcanised rubber, from which 3 per cent. is deducted for combined sulphur. Special methods have to be applied where readily decomposable carbonates, antimony sulphides, or mercury salts, are present. The process should in many cases be useful as a check on the difference method. Another combustion method has been suggested by L. G. Wesson (*J. Ind. and Eng. Chem.*, 1914, **6**, 459; *ANALYST*, 1914, **39**, 568). It consists in preparing a nitrosite and subjecting the latter to combustion. The caoutchouc is calculated from the carbonic acid obtained. The method, originally devised for the analysis of crude rubber, is scarcely likely to be of practical value in the analysis of the vulcanised material. *Indirect (Difference) Methods.*—Considerable attention (*cf.* above) has been paid to the separation of the caoutchouc from fillers by means of solvents. In the absence of the asphalt-bitumen-pitch class of fillers, treatment with a suitable solvent—after extraction with acetone, followed by saponification—must, in most cases, necessarily give a fairly accurate result. The distribution of sulphur may, however, cause some difficulty. Moreover, it should not be forgotten that no process yet devised can distinguish with any certainty between new rubber on the one hand and waste, or reclaimed, rubber on the other hand. The estimation of "rubber" or "caoutchouc" is, consequently, a somewhat illusory problem. By carefully estimating the various non-rubber constituents the experienced analyst will in the majority of cases be able to form a very fair opinion as to the quantity of rubber actually employed in a mixing. If mechanical tests are applicable as well, one can in many cases conclude that not less than a certain proportion of waste or reclaim has been employed.

*Special Problems—Examination of Cable Insulations.*—Rubber mixings are used to a very large extent for the protection or insulation of electric light and power cables. Hitherto no standards of composition or of analysis have been published in this country, but in the United States and in Germany attempts in this direction have been made. In both these countries leading manufacturers, in conjunction with public authorities and experts, appear to have accepted the principle that a rubber mixing for insulation purposes shall contain no ingredients beyond rubber, mineral matter, sulphur, and hydrocarbons of the paraffin series (such as ceresin wax). In the United States a conference of manufacturers, experts, and users (*J. Ind. and Eng. Chem.*, 1914, **6**, 75; *ANALYST*, 1914, **39**, 137), have adopted as a basis a mixing containing not less than 30 per cent. *hevea* (Para, or Plantation "first latex") rubber. Limits are suggested for the waxy hydrocarbons, free and combined sulphur, etc., and detailed methods of analysis have been described. A

German Government institution, in conjunction with a number of cable factories (cf. F. W. Hinrichsen, *ANALYST*, 1913, **38**, 336), have proposed a mixing containing 33·3 per cent. of rubber (containing not more than 6 per cent. of resin) and 66·7 per cent. of fillers, including sulphur. No organic filler excepting ceresin or paraffin wax—to a maximum amount of 3 per cent.—is to be used. Definite methods of analysis, including the separation of fillers by means of a solvent (paraffin oil or camphor oil) have been laid down. Some criticisms of the methods of analysis proposed have appeared. Thus, Britland and Potts (*India-Rubber J.*, 1912, **42**, 333) point out that the method of estimating ceresin proposed gives results which are too low. Moreover, they cannot confirm the work of Hinrichsen and Kindscher (*Chem. Zeit.*, 1910, **34**, 230) in regard to the alleged raising of the acetone extract due to the presence of the waxy filler. F. Jacobssohn (*Gummi-Zeit.*, 1913, **27**, 1906; *ANALYST*, 1914, **39**, 91) criticises, in particular, the suggestion regarding the solvent to be used for the separation of the fillers. *Proofed or "Rubberised" Goods*.—A number of interesting suggestions on the testing of proofed goods are made in a paper by M. B. Setlik and J. Zofka (Eighth International Congress of Applied Chemistry; *ANALYST*, 1912, **37**, 575). A method for estimating lead sulphate in rubber goods is described by J. A. Schaeffer (*J. Ind. and Eng. Chem.*, 1912, **4**, 836; *ANALYST*, 1913, **38**, 44). This substance appears to be used in America in the form of sublimed white lead, a material containing about 78·5 per cent.  $\text{PbSO}_4$ , 16·0 per cent.  $\text{PbO}$ , and 5·5 per cent.  $\text{ZnO}$ . *Direct Determination of Antimony and Mercury Sulphides*.—These sulphides, particularly the former, are very widely used as pigments, and their direct estimation is frequently desirable. Methods for accomplishing this (both based on the principle of destroying the rubber and other organic matter by strong reagents) have been worked out by F. Frank and K. Birkner (*Chem. Zeit.*, 1910, **34**, 49; *ANALYST*, 1910, **35**, 131) and by W. Schmitz (*Gummi-Zeit.*, 1911, **25**, 1928; *ANALYST*, 1912, **37**, 64). The former destroy organic matter by means of fuming nitric acid and ammonium persulphate. The metals are finally weighed as sulphides. If both mercury and antimony are present, separation is effected by dissolving the antimony sulphide by means of carbon bisulphide. Schmitz (*loc. cit.*) uses a modification of the Kjeldahl method for the destruction of organic matter.

