

RUBBER FROM LATEX COAGULATED WITH SULPHURIC ACID

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An article by Wiltshire in the Journal of the Rubber Research Institute, November 1932, p.94, on the use of sulphuric acid as a coagulant of latex has attracted considerable attention amongst rubber manufacturers who have expressed some alarm at the possibility of the extended use of this chemical for coagulation. The India Rubber Manufacturers' Association, Great Britain, stated "it was felt that it is highly undesirable that such a practice should be adopted without first ascertaining that recognised standards of performance, including ageing, will be maintained in the finished manufactured articles".

In view of the apprehensions of manufacturers, samples were supplied by the Rubber Research Institute to the London Advisory Committee in order to investigate as fully as possible the effect on the properties of the rubber of using sulphuric acid as a coagulant

The samples comprised (a) two samples of smoked sheet coagulated with sulphuric acid and formic acid, prepared on a Malayan estate which regularly uses sulphuric acid as a coagulant; and (b) four samples of air-dried sheet prepared by the staff of the Rubber Research Institute. The air-dried sheet samples were in two pairs and were prepared on different days using acetic acid sheet as a control in each case. The sulphuric acid sample in the first pair was prepared using more acid than is usual on estates. Subsequently a further sample of air-dried sheet coagulated with sulphuric acid and prepared on the above Malayan estate was received for comparison with the smoked sheet samples from the same estate.

Particulars of the preparation of these samples are shown in Table I.

All the air-dried sheet samples showed signs of mould, particularly C, E and F.

The samples were divided into two portions, one of which was submitted to tests by the India Rubber Manufacturers'

TABLE I

Sample	Where prepared	Type of sheet	Coagulant.	Amount of Coagulant	D.R.C. of Latex lb./gall.	Other Details
A	A Malayan estate	Smoked	Formic acid	1 fluid oz. to 14.7 lbs. of rubber	1½	9 days smoking
B	A Malayan estate	Smoked	Sulphuric acid	1 fluid oz. to 25 lbs. of rubber	1½	9 days smoking
C	R.R.I.	Air-dried	Acetic acid	2.8 grams per lb. of rubber	1½	Soaked in water 1 hour after machining. Dried 2½ days at 110—120°F.
D	R.R.I.	Air-dried	Sulphuric acid	3.0 grams per lb. of rubber	1½	do.
E	R.R.I.	Air-dried	Acetic acid	2.8 grams per lb. of rubber	1½	do.
F	R.R.I.	Air-dried	Sulphuric acid	2.3 grams per lb. of rubber	1½	do.
G	The same estate as samples A and B.	Air-dried	Sulphuric acid	1 fluid oz. to 25 lbs. of rubber		

Association and the other to the following tests by the staff of the London Advisory Committee:—

Chemical Analysis

Determination of water soluble sulphate present

Plasticity

Hardness (D_{30}) and mastication

Rubber-sulphur mixing (a)

Vulcanisation in 100:10 rubber-sulphur mixing

(b) Ageing in 90 : 10 rubber-sulphur mixing

- Accelerator mixing (a) Vulcanisation and ageing in
 "Captax" mixing
 (b) Vulcanisation and ageing in
 "D.P.G." mixing

The purpose of the chemical test is to indicate whether appreciable amounts of free sulphuric acid remain in the rubber after the coagulum has been machined with the consequent removal of a considerable proportion of the non-rubber serum substances and probably also of the sulphuric acid coagulant.

The purpose of the plasticity tests is to indicate whether the use of sulphuric acid affects the manipulation of the rubber by manufacturers.

Vulcanisation and ageing tests were carried out in three mixings. The rubber-sulphur mixing was selected as one because it gives results which are very sensitive to abnormality in the non-rubber accessory substances and to deterioration of the caoutchouc. The two accelerator mixings selected are more in accord with manufacturing conditions than the rubber-sulphur mixing. Both accelerators are popular, one representing an acidic and the other a basic type of accelerator. They may therefore react differently to traces of sulphuric acid in the rubber. They also differ in that one has antioxidant properties and the other is without effect in this direction. The proportions of the different ingredients in each mixing were selected so as not to hide variability in different samples of rubber and are also in accord with manufacturing practice.

The investigation is considered to be fairly comprehensive from a laboratory point of view, although it does not cover all the points on which manufacturers would possibly like some assurance before approving the extended use of correct proportions of sulphuric acid as a latex coagulant. It is a reasonable presumption however that, if the rubber satisfies all these tests, there is only a remote chance that it will cause difficulty in the rubber factory or shorten the life of the finished article.

CHEMICAL EXAMINATION

Each sample was extracted (Soxhlet extractor) with boiling water for two days and the extract examined for acidity and soluble sulphate in the usual manner, with the result shown in Table II:

The acidity of the aqueous extract of the estate samples is much higher than that of the samples prepared by the Rubber Research Institute. The latter were soaked in water after machining the coagulum to sheet and it is possible that the estate

TABLE II

Sample	Coagulant	Acidity in terms of mg. of KOH per 100 gm. Rubber	Soluble sulphate (SO ₄) per cent.
A	Formic Acid	13.6	0.007
B	Sulphuric "	22.4	0.020
C	Acetic "	4.8	nil
D	Sulphuric "	5.6	trace
E	Acetic "	6.4	nil
F	Sulphuric "	trace	nil

samples did not receive this treatment, which would undoubtedly remove some of the water-soluble material remaining in the rubber.

The amount of free sulphuric acid in the samples prepared by the Rubber Research Institute was so small that it could hardly be detected. There was more soluble sulphate in the estate sample coagulated with formic acid and still more in that coagulated with sulphuric acid. The maximum amount of soluble sulphate in any of the samples was 0.02 per cent, which is no more than might be incorporated with rubber by manufacturers due to the use of slightly acid sulphur or zinc oxide.

These results indicate that the amount of free sulphuric acid remaining in the dry rubber after coagulation with sulphuric acid is not sufficiently large to alarm manufacturers, particularly if the coagulum is soaked in water after machining. It is possible to use excess of sulphuric acid for coagulation and only a trace may be apparent in the dry rubber after machining and soaking the coagulum.

PLASTICITY

The results of plasticity tests are given in Table III.

TABLE III

Sample	Coagulant	D ₃₀ (mm.)	Mastication No.
A	Formic	1.56	104
B	Sulphuric	1.49	108
C	Acetic	1.51	110
D	Sulphuric	1.42	97
E	Acetic	1.51	113
F	Sulphuric	1.42	100

The samples prepared with sulphuric acid are, in general, slightly softer than the control samples and masticate on the whole more easily. It appears likely therefore that the use of sulphuric acid will have an advantageous effect as regards the manipulation of rubber by manufacturers.

VULCANISATION AND AGEING

The results of vulcanisation and ageing tests are shown in the Tables IV to VIII.

Table IV Series of cures in rubber-sulphur mixing 100 : 10.

Table V Ageing tests in vulcanised rubber-sulphur mixing 90 : 10.

Table VI Range of cures in a Captax mixing.

Table VII Ageing tests in a Captax mixing.

Table VIII Ageing tests in a D.P.G. mixing.

There is no evidence that the sulphuric acid samples are weaker than the controls on vulcanisation in the rubber-sulphur or accelerator mixings. In all the mixings the sulphuric acid samples on ageing retain their strength for approximately the same period as controls. In some cases the controls are a little better than the sulphuric acid samples and in others the latter have the advantage.

TABLE IV

Mixing : Rubber ... 100
Sulphur ... 10

Sample	Tensile Strength (lb./sq. in.) after Vulcanisation at 148°C for			Elongation per cent at Load of 1.04 kg./ sq.mm. after Vulcanisation at 148°C for			Calculated correct Time of Cure, i.e. to give Elong = 800. (min.)
	120 min	140 min.	160 min.	120 min	140 min.	160 min.	
A Smoked sheet Formic acid	1960	2130	—	883	797	—	139
B Smoked sheet Sulphuric acid	1850	2250	—	889	789	—	138
C Air-dried sheet Acetic acid	1910	2330	—	870	794	—	138
D Air-dried sheet Sulphuric acid	1180	2140	2340	930	853	800	160
E Air-dried sheet Acetic acid	1740	1950	—	893	810	—	142
F Air-dried sheet Sulphuric acid	1230	1710	2350	915	843	792	158
G Air-dried sheet Sulphuric acid	2400	2500	—	840	766	—	131

TABLE V

Mixing : Rubber ... 90
Sulphur ... 10

Sample	Time of Vulcanisation at 148°C. (min.)	Tensile Strength (lb./sq.in.) after Ageing at 70°C for Hours							Elongation (per cent) at Load of 1.04 kg./sq.mm. after Ageing at 70°C for Hours						
		0	48	96	120	144	168	192	0	48	96	120	144	168	192
A Smoked sheet Formic acid	106	1890	2520	2250	2100	1730	1930	1650	857	774	738	722	706	695	677
B Smoked sheet Sulphuric acid	106	1880	2560	2020	2160	1850	1600	1280	864	782	748	720	708	692	—
C Air-dried sheet Acetic acid	107	1830	2130	1740	1490	360	—	—	874	780	729	710	—	—	—
D Air-dried sheet Sulphuric acid	125	1990	2210	1920	1860	1550	—	—	888	796	748	724	725	—	—
E Air-dried sheet Acetic acid	115	2030	2530	2100	2070	460	—	—	853	762	706	692	—	—	—
F Air-dried sheet Sulphuric acid	125	1900	2130	1830	1460	250	—	—	875	783	731	712	—	—	—

TABLE VI

<i>Mixing : Rubber</i>	...	100
<i>Zinc oxide</i>	...	6
<i>Sulphur</i>	...	3.5
<i>Stearic acid</i>	...	1
<i>Captax</i>	...	0.5

Sample	Tensile Strength after Vulcanisation at 126°C for					Elongation at Load of 1.04 kg./sq.mm. after Vulcanisation at 126°C for				
	20 min.	40 min.	60 min.	80 min.	100 min.	20 min.	40 min.	60 min.	80 min.	100 min.
A Formic acid Smoked sheet	1180	1830	2320	2410	2280	—	849	775	741	744
B Sulphuric acid Smoked sheet	1000	2030	2030	2540	2360	—	849	788	743	746
C Acetic acid Air-dried sheet	1120	1590	2050	2280	2310	—	884	808	784	783
D Sulphuric acid Air-dried sheet	1280	2090	2430	2570	2390	—	843	794	767	761
E Acetic acid Air-dried sheet	730	1770	2080	2080	2160	—	890	867	807	810
F Sulphuric acid Air-dried sheet	240	1430	1920	2120	2330	—	—	905	860	847
G Sulphuric acid Air-dried sheet	1200	2210	2300	2350	2360	—	837	796	766	763

TABLE VII

Mixing : Rubber ... 100
 Zinc oxide ... 6
 Sulphur ... 3.5
 Stearic acid ... 1
 Captax ... 0.5

Sample	Time of Vulcanisation at 126°C (min.)	Tensile Strength (lb./sq in.) after Ageing at 82.5°C for Days							Elongation (per cent) at Load of 1.04 kg./sq.m.m. after Ageing at 82.5°C for Days						
		0	2	4	6	8	10	12	0	2	4	6	8	10	12
A Formic acid Smoked sheet	80	2290	2770	2480	1840	500*	960	230	736	629	616	575	—	—	—
B Sulphuric acid Smoked sheet	80	2650	2330	2770	2330	1990	1560	740	734	664	642	613	574	560	—
C Acetic acid Air-dried sheet	80	2430	2770	2340	2150	1630	1520	750	771	663	651	623	587	563	—
D Sulphuric acid Air-dried sheet	80	2320	2550	2030	2340	850	890	200	721	660	653	619	—	—	—
E Acetic acid Air-dried sheet	80	2120	2570	2430	1980	1810	1370	710	775	690	681	644	626	603	—
F Sulphuric acid Air-dried sheet	100	2220	2140	2100	1690	1190	710	190	776	725	719	683	—	—	—
G Sulphuric acid Air-dried sheet	80	2650	2500	2200	1560	390	235	250	731	644	633	596	—	—	—

*Probably two exceptionally weak rings

TABLE VIII

Mixing : Rubber ... 100
 Zinc oxide ... 6
 Sulphur ... 2.75
 D.P.G. ... 0.1

Sample	Time of Cure. at 141°C. (min.)	Tensile Strength (lb./sq in.) after Ageing at 82.5°C for Days						Elongation (per cent) at Load of 1.04 kg./sq.mm. after Ageing at 82.5°C for Days					
		0	2	4	5	6	7	0	2	4	5	6	7
A Formic acid Smoked sheet	60	2050	2500	1500	1060	510	260	787	744	777	—	—	—
B Sulphuric acid Smoked sheet	60	2580	2400	1550	1450	1000	200	752	718	740	740	—	—
C Acetic acid Air-dried sheet	60	2450	1640	1200	1110	250	170	735	694	730	—	—	—
D Sulphuric acid Air-dried sheet	60	2160	2270	1460	1400	915	430	770	735	764	774	—	—
E Acetic acid Air-dried sheet	60	1980	2120	1250	1180	740	340	774	723	753	—	—	—
F Sulphuric acid Air-dried sheet	60	2370	2200	1160	660	160	170	795	762	780	—	—	—

The sulphuric acid coagulated air-dried sheets prepared at the Rubber Research Institute required approximately 14 per cent. longer vulcanisation than the controls in rubber-sulphur mixings, but the rate of vulcanisation of the smoked sheet and air-dried sheet prepared on a Malayan estate is hardly affected by the use of sulphuric acid. The latter results are contrary to general experience, and in a number of cases it has been observed that the estate samples differ in their relative behaviour from those prepared at the Rubber Research Institute. It is possible that the estate samples are abnormal and that definite conclusions should be confined to those drawn from the results given by the Rubber Research Institute samples.

In the Captax mixing there is little difference between the estate samples, but the two pairs of air-dried sheets from the Rubber Research Institute show small differences which are in opposite directions.

In the D.P.G. mixing the air-dried sulphuric acid sheets prepared at the Rubber Research Institute give a softer vulcanisate than the controls, but the estate smoked sheet displays the opposite effect.

In the Captax mixing the sulphuric acid samples display a smaller increase in modulus during ageing than the other samples. This is an advantage but it is not important and is not displayed in the other mixings.

It appears from these results that the most important effect of the use of sulphuric acid is an alteration in rate of vulcanisation, particularly in the rubber-sulphur mixing, and it is evident that the use of sulphuric acid on some estates and of acetic and formic on other estates must tend to increase variability and thereby prejudice manufacturers against the use of first-grade rubber.

The effect of the sulphuric acid when used in correct proportion is very small, however, when compared with the total variability which already exists. The rubber from some estates using formic or acetic acid as a coagulant may vulcanise twice as fast as that from others using the same coagulant, whereas the retardation of vulcanisation owing to the use of sulphuric acid is less than 20 per cent. and may in some cases be much less.

In the case of accelerator mixings the effect of using sulphuric acid cannot be measured in terms of rate of vulcanisation owing to the slow alteration in physical properties with period of vulcanisation, but the limited data available indicate that the use of sulphuric acid would lead to an increase in variability which is small compared with that already existing in rubber from different estates.

The India Rubber Manufacturers' Association arrived at similar conclusions from the results of their tests on portions of the samples. Their report is as follows:—

“With regard to the rubber coagulated with sulphuric acid it was found that, in every case, the rubbers so coagulated were slower curing than the standard rubbers in pure rubber stocks not containing added accelerator. When adjustment was made for this slowing-up in curing the ultimate physical properties of the above were satisfactory.

When stocks were used containing accelerators different results were obtained depending on the choice of the accelerator. With an accelerator of the type of mercaptobenzothiazole increased activation was obtained in the case of rubbers coagulated with sulphuric acid whilst in the case of accelerators such as D.P.G., where best results obtained with alkaline conditions, retardation was again found.

It was again found that when these factors were recognised and the articles cured to an equivalent state of cure, similar ageing properties were obtained. It would, therefore, appear from the tests carried out that coagulation with sulphuric acid under properly controlled conditions could give rubbers with intrinsic properties equal to those obtained with standard methods of preparation. Our tests, however, do suggest that a rubber manufacturer who unwittingly received a substantial part of his deliveries in the form of rubber coagulated with sulphuric acid might encounter definite manufacturing trouble due to the rate of vulcanisation being abnormal, and due to the fact that variable results would obtain according to the type of accelerator being used and the type of article being manufactured.

We think that you will realise that owing to the small size of the samples sent, only laboratory tests could be carried out, and it was not possible to make a variety of manufactured articles which could be put to service tests. The tests, however, do serve to show that the use of sulphuric acid requires very careful consideration on the part of rubber growing interests, and they do definitely indicate the possibility of normal manufacture being thrown out of gear due to the properties of the sulphuric acid coagulated rubber being abnormal with regard to cure.

We therefore advise that rubber coagulated with sulphuric acid should not be put on the market without the method of coagulation being definitely stated.”

Summary

The results of tests carried out in the laboratories of the London Advisory Committee show that when sheet rubber is prepared by coagulation of latex with sulphuric acid

- (1) only a trace of free sulphuric acid remains in the dry rubber,
- (2) the rubber is somewhat easier to manipulate in rubber manufacturing operations than that prepared by coagulating latex with acetic acid,
- (3) the rubber has satisfactory mechanical properties when vulcanised in rubber-sulphur or accelerator mixings,
- (4) the rubber ages satisfactorily in rubber-sulphur and accelerator mixings,
- (5) the use of sulphuric acid would tend to increase the variability in vulcanisation of first-grade rubber unless its use became general.

Conclusions

The use of correct proportions of sulphuric acid as a coagulant is not harmful to the intrinsic properties of the rubber. On the other hand the economy due to its use is not large (.014d. per lb. rubber) and there is a possibility of harm arising in two directions, viz.

(1) As long as it is used by only a proportion of estates it will increase slightly the variability of rubber and so tend to prejudice all manufacturers against first-grade rubber in favour of lower grades in which a high degree of uniformity cannot reasonably be expected. There is no doubt that some manufacturers view with apprehension the possibility of an increase, however slight, in the variability of first-grade rubber. In addition, manufacturers of high grade special articles would be unwilling to use on a large scale rubber which they knew had been coagulated with sulphuric acid unless they first had an opportunity of making prolonged and thorough tests with their own products.

(2) The accidental use of excess of sulphuric acid, in addition to causing difficulty on an estate, is known to have a definitely harmful effect on the rubber. The use of excess of acetic or formic acid has no serious effect on the properties of the rubber.

It is not anticipated that the plantation industry would suffer serious disadvantage from the general use of sulphuric acid as a coagulant, but the economy does not appear to be sufficient to justify the risk, especially in view of the objections raised by manufacturers.

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