THE
BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION

Publication No. 175

COLD MASTICATION OF RUBBER

by

W. F. WATSON

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~~IRI Transactions~~

IRI Transactions 29(1) 1953: 32-41

Reprinted from I.R.I. TRANSACTIONS, Vol. 29, No. 1.

Cold Mastication of Rubber

BY W. F. WATSON, Ph.D., D.Sc.

SUMMARY

The processes underlying the plasticising of rubber by cold and hot mastication are of different chemical types. In hot mastication, plasticising is caused by oxidative reactions. In cold mastication, plasticising is due to a primary rupture of the long chain rubber molecules by the applied deformation forces and a secondary consummation of this rupture by oxygen or other compounds reactive towards the ruptured chains. Alternative to consummation of rupture, certain compounds thereby initiate cross-linking. Experimental results are quoted in support of this interpretation of cold mastication processes and some practical conclusions drawn.

One of the commonest operations in the rubber industry is the softening of its basic raw material by milling on open mills or by masticating in an internal mixer. Although in practical use for nearly one hundred years, with improvements in machines and the introduction of so-called chemical peptisers giving ever-increasing efficiency, the nature of the fundamental process involved has remained largely unknown. Perhaps the only generally accepted feature is that plasticisation reflects

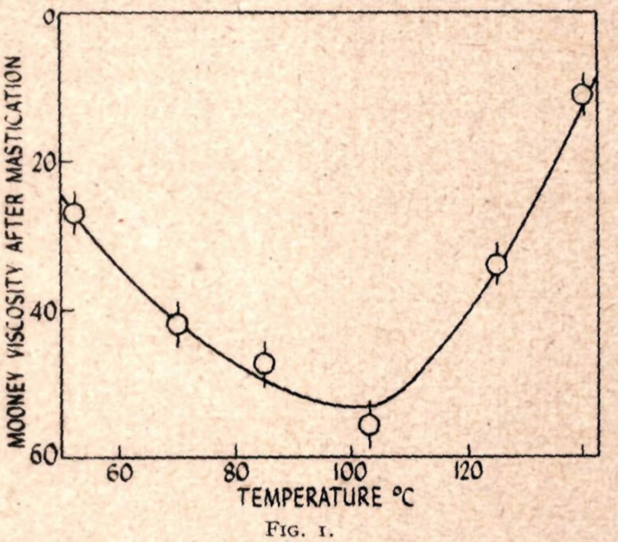

FIG. 1.

Efficiency of mastication in air at different temperatures as shown by the Mooney viscosity of the rubber after 30 minutes mastication. Initial rubber—U.S.F. grade of Mooney viscosity 80.

a net reduction in size of the very large molecules, and therefore that the plasticising processes are to be satisfactorily explained in precise terms only by chemical reactions specificially accounting for this molecular breakdown.

Two experimental observations which provide important clues as to the nature of the breakdown processes are (i) the unusual temperature dependence (Fig. 1[cf.1]), and (ii) *the apparent necessity for the presence* of oxygen (Fig. 2*). In view of the known oxidisability of rubber hydrocarbon and allied substances, it is reasonable to regard the right-hand branch of the U-shaped curve of Fig. 1—that is, the increasing susceptibility to breakdown with temperature above *ca.* 100° C.—as intimately associated with oxidiation.[2] The increase in breakdown at the higher temperatures is comparable with increase in oxidation and

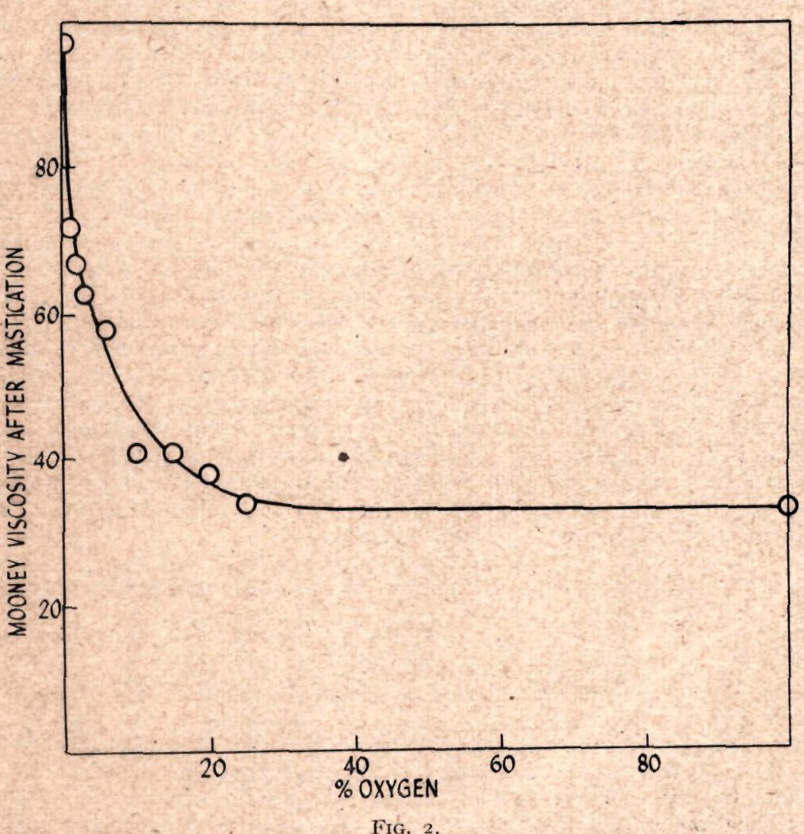

FIG. 2.

Influence of oxygen concentration on the efficiency of mastication after 20 minutes of smoked sheet of initial Mooney viscosity 93.

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* It was suggested by Dr. C. M. Blow that these unpublished results of Mr. R. I. Wood and himself be reported here.

the rate of breakdown responds as expected to the presence of oxidation catalysts and retarders.

More difficult to explain is the left-hand branch of the U-curve. Not only is the negative temperature coefficient of the process responsible for softening in this region anomalous in relation to ordinary chemical reactions, but two other curious facts require interpretation, viz. (*a*) though oxygen is necessary, oxidation retarders have little effect on breakdown in this temperature region; (*b*) different rubbers, natural and synthetic, undergo breakdown at comparable rates, although their oxidisabilities are widely different. Various *ad hoc* assumptions advanced to account for the negative temperature coefficient, and sometimes also for (*a*) and (*b*), have mainly involved modifications of the oxidative process considered to apply at higher temperatures. However, no independent evidence to support any of these assumptions has been forthcoming.

Among these various speculations exists a significant contribution by Kauzman and Eyring.[3] They suggested that under conditions of cold mastication the intense shearing forces imposed on the stiff rubber suffice to rupture primary chemical bonds of the long-chain molecules. The polymer fragments produced are assumed not to be two long-chain molecules but two very reactive free radicals which must almost immediately engage in some stabilising reaction converting them to molecules. In an inert atmosphere such as nitrogen, this stabilisation is most easily realised by the radicals recombining with themselves—thereby accounting for the experimental result of no observable overall breakdown. In oxygen, on the other hand, an alternative course of comparable facility is available, namely, the addition of oxygen to the radical ends to produce oxygenated radicals which stabilise themselves by side-reactions. The theory may be schematically represented by:

$R\text{—}R \longrightarrow R\cdot + R\cdot$ mechanical rupture into free radicals (1)
$R\cdot + R\cdot \longrightarrow R\text{—}R$ radical recombination (2)
$R\cdot + O_2 \longrightarrow RO_2\cdot$ oxygen intervention (3)
$RO_2\cdot \longrightarrow\!\!\!\!\!\rightarrow$ stable molecule breakdown stabilisation (4)

In nitrogen, reactions (1) and (2) alone are operative; in oxygen, reactions (3) and (4) occur and are responsible for the permanence of breakdown. Softening by cold mastication is then adequately explained, but this explanation, like others, has remained unsubstantiated by more critical experiments.

It is important to recognise that, according to Kauzman and Eyring's theory, oxygen plays what may be termed a passive rôle in the breakdown at temperatures below about 100° C.—it merely intervenes to repress the recombination after molecular rupture has been achieved mechanically—in contrast to its active oxidative rôle at higher temperatures. This being assumed, it is reasonable to expect that many other additives could replace oxygen in consummating breakdown, the essential requirement being that they can react readily with hydrocarbon radicals. Possible substances can be selected from a knowledge of their reactivities towards free radicals in other systems. A typical example is benzoquinone, Q, and, in conformity with our ideas, it does function as a breakdown agent on masticating *under nitrogen* at temperatures below 100° C. in a parallel manner to oxygen (Fig. 3). The difference between the oxygen and benzoquinone curves signifies that reaction (3′) is not able to compete so effectively with recombination as reaction (3).

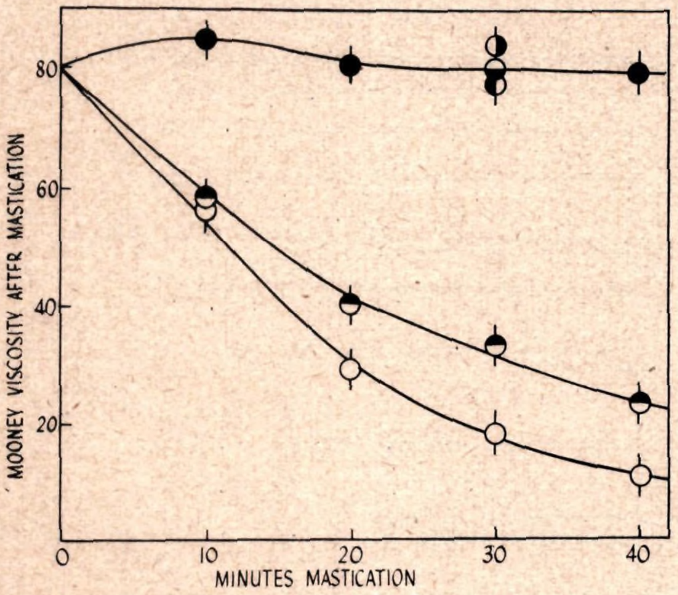

FIG. 3.

Mastication in air and nitrogen with and without benzoquinone.
Initial rubber—U.S.F. grade of Mooney viscosity 80.

- ● masticating in nitrogen.
- ◓ masticating in nitrogen with 1 gm. benzoquinone/100 gms. rubber (0·0925 m./1000 gms.).
- ◐, ◓, ◑ masticating in nitrogen with 0·0925 m./1000 gms. of ethylacetate, dibutylether, and *iso*propyl alcohol respectively.
- ○ masticating in air.

$$R- + Q \longrightarrow RQ- \qquad \text{benzoquiqone intervention} \qquad (3')$$

In fact, of forty-seven compounds so far tested and found to produce observable breakdown on masticating under nitrogen, not one exceeds oxygen in efficiency and most are much inferior. This is illustrated in Fig. 4, where the Mooney viscosities after mastication with some of these compounds are given together with a pictorial representation of the shortening of the rubber molecules.

From similar considerations many substances would be expected to be inert towards rubber radicals, and so to be ineffective in promoting breakdown during mastication under nitrogen. Typical members of several large classes of compounds suggest, in conformity with wider experience, that alcohols, ethers, ketones, esters and hydrocarbon oils act merely as neutral diluents under these conditions (e.g. Fig. 3).

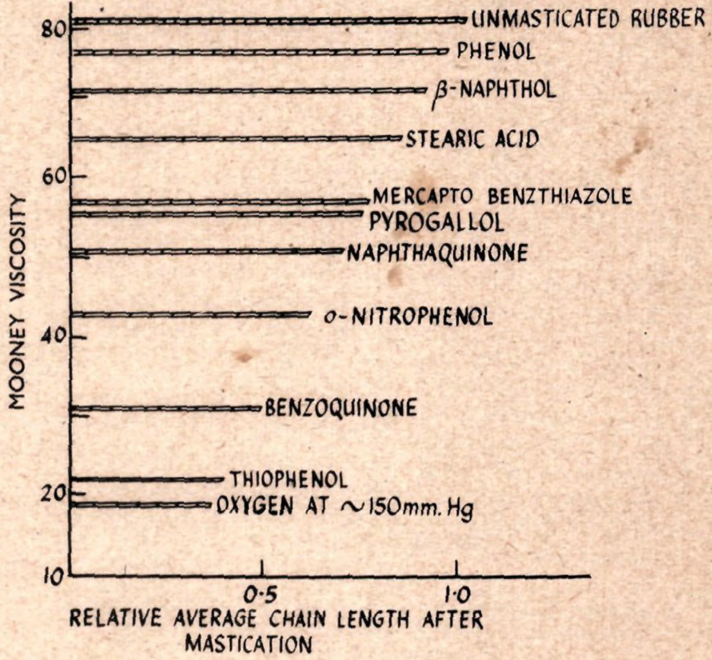

FIG. 4.

Efficiency of various compounds in stabilising breakdown on 30 min. masticating under nitrogen.

A disadvantage of using oxygen to study breakdown initiated by mechanical rupture is the overlapping softening action by oxidative scission (Fig. 1). Most other breakdown agents do not possess such a dual activity, and thus make it possible to obtain only the left-hand branch of the softening-temperature curve (e.g. Fig. 5). This seems the clearest demonstration of the essentially different nature of the softening processes predominant at low and high temperatures. The factors influencing the shape of the cold mastication curve are the shearing forces imposed on the rubber by the masticating machine, the stiffness of the rubber, and the efficiency of the substance consummating breakdown, as illustrated in Fig. 5.

Although the rate of breakdown under cold mastication conditions is controlled by the rate of mechanical rupture and the relative rates of recombination and the competitive reaction of type (3), the nature of the product obtained is largely determined by what happens to consummate breakdown in reactions of type (4). Several possibilities exist: (i) the free radicals may be converted to stable molecules of the same chain length, producing softened rubbers identical in physical properties to those of the rubber masticated in air to the same extent of breakdown

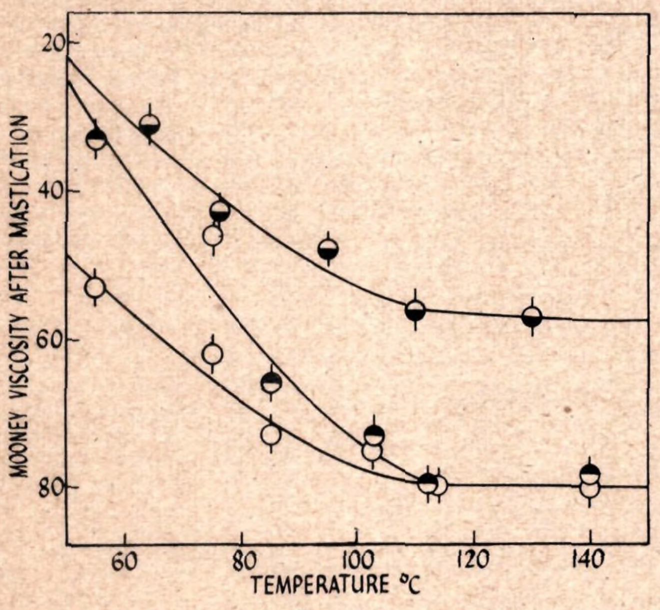

FIG. 5.

Efficiency of mastication under nitrogen at various temperatures in the presence of benzoquinone and azobenzene.

◒ U.S.F. rubber of initial Mooney viscosity 57, with 1 gms./100 gms. benzoquinone.

◓ U.S.F. rubber of initial Mooney viscosity 80, with 1 gm./100 gms. benzoquinone.

○ U.S.F. rubber of initial Mooney viscosity 80, with 1·82 gms./100 gms. azobenzene.

(e.g. the substances of Fig. 3 give rise to rubbers of this type). (ii) The free radicals may attack other rubber molecules and so finally produce a branched-chain polymer. This behaviour is of particular interest because branched but soluble rubbers are otherwise difficult to produce. Compounds functioning at least partly in this way are *n*-butyramide, aniline, azo*bis*isobutyronitrile, and *m*-nitrophenol. (iii) The radicals may attack rubber molecules and thereby initiate a cross-linking reaction. The result is then a rubber of high Mooney viscosity and gel content. The most potent cross-linking agent found was chloranil, which produced a rubber crumb of 80 per cent. gel content. Another rubber of this type is so-called "anhydride" rubber[4], obtained by masticating under nitrogen or air in the presence of maleic anhydride or acrylonitrile.

In contrast with the action of the above substances, physical-softening agents for rubber should decrease the rate of mechanical rupture by decreasing the shearing forces and not greatly influence the subsequent chemical reactions. Typical softness did, in fact, not produce observable breakdown of the rubber on masticating in nitrogen; with benzoquinone added, the results of Table I were obtained. The practically-useful result emerges that the rubber has been as efficiently degraded in the presence of the softeners. Softeners decreased the temperature of the masticating rubber by reducing internal friction, and so, consistent with the mechanism proposed, rubber with softener at the same temperature is less degraded than the rubber alone. It is, however, surprising that the influence of softeners give such a quantitative compensation as noted in Table I.

TABLE I

MASTICATION WITH BENZOQUINONE UNDER NITROGEN OF RUBBERS AFTER INCORPORATION OF SOFTENERS

Initial Mooney Viscosity of U.S.F. Rubber—80 ± 3

Concentration of Benzoquinone 0·0925 m./1000 gms. rubber

Time of mastication—30 mins.

Temp. of water-flow through the Banbury Mixer—14° C.

Liquid	Conc. of Liquid gm./100 gms. rubber	Mooney Viscosity of Masticated Rubber after Acetone Extraction
Mineral Oil	0	36*
	10	36
	15	37
	23	37
	0	28†
Dibenzyl Ether	5	31
	10	28
Acetophenone	5	32
	10	26
Dibutyl phthalate	5	29
	10	26

* The Banbury Mixer was not at normal masticating efficiency for the series of experiments with Mineral Oil.

† This is the comparative mastication of rubber without softener for the subsequent data.

Although as yet little investigated, the general features of plasticising of synthetics are in accord with the above scheme proposed for natural rubber. The several synthetic rubbers tested do not soften on mastication alone in nitrogen at low temperatures, but do so on the addition of compounds effective with natural rubber. Important differences are noted in the relative rates of the different reactions; in particular, oxygen is comparatively inefficient with synthetic rubbers. The mode of action of many peptisers for softening synthetic rubber during mastication appears to be by the mechanism now advanced and not, as commonly supposed, by their functioning as oxidation catalysts.[5] As most synthetic rubbers are less oxidisable, mechanically-induced breakdown is probably important to temperatures higher than with natural rubber.

Summing up, this theory of the cold mastication process appears to collect into a coherent picture many of the diverse phenomena of milling and masticating in an internal mixer. The essential factors for efficient softening at low temperatures can be explicitly stated, namely (*a*) a masticator providing high rates of shear and (*b*) the presence of a compound preventing the recombination of ruptured chains. A rational hypothesis is now available to direct investigation into the use of mastication as a versatile method for producing, as well as softer rubber, rubbers which are more viscous but soluble (branched) and rubbers of varying degrees of gel content (crosslinked). The concepts of chain rupture and recombination, and the associated chemical reactivity towards rubber radicals appear likely to be fruitful in other directions, e.g. in ameliorating certain ageing effects, in reinforcement, and in explaining some of the deterioration occurring on flex-cracking[6] and other rapid and severe deformation.

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[*Received* 10*th July*, 1952.]

DISCUSSION

At a meeting of the London Section of the Institution of the Rubber Industry, held at 26, Portland Place, W.1, on 12th February, 1952, the above paper was read by Dr. Watson.

Mr. W. F. O. POLLETT said that he had been particularly interested in the paper because it bore some relation to tests he had carried out mainly on plastics, but including a few on rubber. In these rubber sheared in a rheometer at about 100° C. showed only small changes in shear stress but the normal stress component fell rapidly. It seemed possible, therefore, that if viscosity was used by Dr. Watson as the only criterion of breakdown he may in fact have concluded that there was no effect when change in elastic properties had in fact occurred.

Dr. WATSON, replying, said that almost no change was observed in Mooney viscosity on masticating under nitrogen. According to the present view of rupture and recombination under these conditions, the overall number-average molecular weight should remain constant. As the Mooney viscosity of gel-free rubber seems to depend mainly on number-average molecular weight, its constancy is expected. However, as pointed out by Mr. Pollett, a change in chain length distribution would be expected by this random rupture and recombination, which would show up by measurements more sensitive to distribution changes. The chain distribution changes can be calculated, and it is hoped will later provide further data relevant to the cold mastication mechanism.

Dr. S. H. MORRELL asked whether any work had been done with butyl rubber in the present series of experiments?

Dr. WATSON replied that no mastication experiments had been done with butyl rubber. As it is among the least oxidisable of synthetic rubbers, it is likely that plasticising is mainly by a mechanical-rupture process.

Mr. J. M. BUIST remarked that Dr. Watson had presented a clear and concise picture of what occurred during the mastication of natural rubber. The mechanism he advanced also seemed to fit the case of GR–S as some preliminary experiments with GR–S carried out at Blackley gave results in general accord with those reported here for natural rubber. For example, the lower efficiency of oxygen than of thiophenol and benzoquinone, is confirmed. The stiffening of GR–S on mastication has often been debated and in fact some authorities have questioned whether it was possible for GR–S to stiffen on mastication. Dr. Watson had explained that under oxygen deficient conditions there is a greater competition between radical-polymer reactions and recombination than occurs with natural rubber.

Mr. A. Cooper said that they were all familiar with the toughening of masticated rubber during storage. It appeared to him that in this work where the reaction of the ruptured ends of the rubber molecule is stopped by these reactive chemicals, such toughening would be inhibited. If this were so we had here a most important practical application of this work in our factories.

Dr. Watson answered that the cause of toughening of masticated rubber in storage is unknown. Among other possibilities, it may proceed by a free radical mechanism. If so, it is probable that it can be reduced by adding materials which are reactive during cold mastication.

Dr. J. R. Scott enquired whether Dr. Watson had studied the form of the relationship between the efficiency of cold mastication and the viscosity at the particular temperature used? As mechanical breaking of the rubber chains is caused by viscous forces, some simple relationship would be expected. Also, does the temperature at which "efficiency" become zero depend on the rate of shear used in milling the rubber? Such a dependence would be expected, the temperature being higher the higher the shear rate.

Dr. Watson replied that as Dr. Scott had suggested, a relationship between efficiency of mastication and viscosity of the rubber at the temperature of mastication might be expected. The Mooney viscosities of rubber at various mastication temperatures were measured. No simple relationship was apparent, the Mooney value decreasing with rise in temperature according to quite a different function of the temperature compared with efficiency of mastication. It was concluded that this was probably due to the Mooney viscosity measured at low rates of shear not being comparable with the high rates of shear in the mixer.

The temperature at which the efficiency of mastication is smaller than the experimental error of its measurement by Mooney viscosity would be anticipated to vary as suggested in the question. However, the Banbury mixer was only operated at one speed, and so this was not tested. The complementary question of attaining higher temperatures for zero efficiency of mastication with more viscous rubber can be answered positively.

Mr. G. N. Welding asked if Dr. Watson had tried detecting fragments of the radical attacking reagents combined in the rubber, such as S from thiols and whether the addition of a polymerisable monomer such as styrene had been tried as a means of detecting from the resultant polymerisation the production of radicals in nitrogen?

Dr. Watson said that radio-active tracer methods are at present being investigated in an attempt to answer the first part of the question and to the second, that a monomer such as styrene had not been used. It is probable that the radicals produced by rupture are of the allylic type, which are very unreactive towards the double bonds in polymerisable monomers.

Dr. F. S. Breuer asked whether, in view of the electronegative nature of most of the chemicals used for stopping recombination of the formed free radicals, they could be arranged according to some principle such as dipole moment, or was it only possible to proceed empirically?

Dr. Watson answered that the choice of probably reactive chemicals was semi-empirical, in that they were chosen for their known reactivity in other free radical systems. There has been no successful attempt as yet to list reactivity towards free radicals by a single property such as dipole moment.

Mr. N. C. H. Humphreys said that in one of the tables, stearic acid was shown to bring about a change in plasticity in the absence of oxygen. Why did the fatty acids normally present in rubber not show this effect in other parts of the work? Was extracted or otherwise specially prepared rubber used to prevent this effect?

Dr. Watson replied that as unpurified smoked sheet and "F" rubber were not plasticised by cold mastication under nitrogen, the chemical nature or concentrations of the acids and other non-rubber constituents did not cause them to function detectably during mastication. Less pure rubber, such as blanket crepe, did plasticise under nitrogen due to adventitious reactive chemicals.

Communicated. The total acid contents of the smoked sheet and "F" rubber were respectively equivalent to 0·030 and 0·032 moles/1000 gms. monobasic acid. Stearic acid at 0·09 moles/1000 gms. decreased the Mooney viscosity on 30 mins. mastication by only 10 units in 75, and so the quantity naturally present would have no effect greater than the experimental error.

This question raises another point. Blow and Wood (*Trans. I.R.I.*, 1950, **25**, 309) maintained that stearic acid acted as an internal lubricant for raw rubber. Dr. Blow suggested that these opposing hypotheses would be tested by measuring the decrease in viscosity after different periods of cold mastication under nitrogen, a lubricant giving a rapid initial plasticising to a constant value, but a radical reactant giving more continuous plasticising. The following results with smoked sheet show that stearic acid is not an internal lubricant:—

Minutes mastication	0	10	20	31
Mooney viscosity	86	83	81·5	76