

MOONEY VISCOSITY CHANGES IN FRESHLY- PREPARED RAW NATURAL RUBBER

BY

R. I. Wood

Summary

In the course of investigations carried out in connection with the Technical Classification of Natural Rubber large permanent increases in Mooney viscosity of the order of 30 to 40 units have been observed when freshly-prepared raw or masticated rubber is stored under conditions of low relative humidity.

The rate of change and the extent of the increase are both affected by the relative humidity of storage, the effects being most marked in the region below about 30 per cent R.H. Rate of change in dry air increases with decreasing sample thickness and with increasing temperature, although the effects are masked somewhat by oxidative breakdown on prolonged storage at temperatures higher than about 30° C.

Mooney values continue to increase long after the rubber has reached constant weight on drying; the removal of acetone soluble and nitrogenous non-rubber constituents and of oxygen does not prevent the changes taking place. The effects are only partially reversed by subsequent storage at high R.H., and there is evidence to suggest that the hardening is associated with the development of a cross-linked benzene-insoluble gel structure throughout the rubber.

The rate of mill-breakdown of dry stored rubber is greater than for fresh rubber, but in comparisons using a fixed breakdown procedure the hardened rubber still has a higher Mooney value after mastication. Rubbers hardened by dry air storage exhibit slightly improved vulcanised properties in a pure gum mix even after the additional breakdown required to reach normal stock viscosity levels.

Fluctuation of temperature and humidity in commercial smokehouses and drying sheds may well account for part of the variability of natural rubber as measured by Mooney viscosity determinations on the freshly-prepared product, and different conditions of storage will add a further contribution to the total hardness variation experienced by the consumer.

Introduction

In the scheme for the technical classification of natural rubber, assessment of processability has been based on Mooney viscosity determinations on the freshly-prepared raw material (1). Consumer evaluations of supplies of Technically Classified Ribbed Smoked Sheet from the Far Eastern producing areas have shown, however, that this method is not particularly satisfactory, due in part to the increases in Mooney viscosity which occur between initial testing in the producing areas and use by the consumer (2).

In 1927 de Vries (3) reported changes in hardness of first grade rubber on storage, and associated hardening and softening respectively with an excess or deficiency of serum substances. Investigation into the effect of different storage conditions upon the hardness of raw rubber were carried out by Martin and co-workers (4) in 1930-31 and they concluded, *inter alia*, that temperature of storage, complete absence of moisture and presence of oxygen all had a permanent effect on the hardness of rubber as measured by a parallel plate plastimeter. More recent work by various investigators (5) has confirmed that the Mooney viscosity of 'old' rubber (*i.e.* rubber as received by the consumer after normal shipment from the producing areas) can be varied by some four to ten units, depending on whether it is stored at high (98 per cent) or low (0 per cent) humidity for a further period.

From the point of view of any classification scheme based on measurements of Mooney viscosity, the important changes are those which take place between the testing of the freshly-prepared rubber under tropical conditions and its use by the consumer after storage, usually in a temperate climate. Wren (6) has observed increases of the order of 25 Mooney units for freshly-prepared R.S.S. when stored for three months over calcium chloride, as compared with increases of about five units when stored for the same period in the laboratory under tropical conditions, and the work reported in this paper covers some of the conditions which influence Mooney viscosity and hardness changes in fresh rubber during subsequent storage. It was carried out mainly for the purpose of obtaining information on Mooney viscosity changes on storage in connection with the scheme for the technical classification of natural rubber and is presented here not as a completed investigation, but as a series of observations which it is hoped may serve to indicate the lines of development of further research.

Sample Preparation and Test Methods

The rubbers used throughout were freshly-prepared (*i.e.* tested not later than two weeks after preparation) Ribbed Smoked Sheet or Air-dried Crepe. For each experiment a homogenised mass was obtained by mill blending, using six passes between the cold rolls of a 12 inches \times 6 inches laboratory mill, at friction ratio (1 : 1.4), the sample being rolled and up-ended between passes. It had previously been established that this method gave satisfactory blending with a minimum of breakdown of the raw rubber. After blending, samples were sheeted out to the desired thickness by one additional pass.

TABLE 1

Days of Storage	Stored over Calcium Chloride			Laboratory-stored		
	Raw Mooney Viscosity	Change in Weight	Further Change in Weight of Stored Sample on oven-drying	Raw Mooney Viscosity	Change in Weight	Further Change in Weight of Stored Sample on oven-drying
0	74.0			74.0		
1		-0.28%			+0.09%	
2	78.5	-0.34%	-0.10%			
3		-0.36%				
4	84.0	-0.37%	-0.09%	73.5	+0.14%	-0.56%
5		-0.37%				
6	89.5	-0.37%	-0.09%			
7		-0.38%				
8		-0.39%				
9		-0.37%				
10	95.0	-0.38%	-0.12%	75.5	+0.18%	-0.62%
15	100.0	-0.38%	-0.07%	75.0	+0.19%	-0.59%
20	103.0	-0.38%	-0.10%		+0.20%	
25		-0.37%			+0.21%	
31	108.0	-0.37%	-0.07%	74.0	+0.17%	-0.59%

TABLE III

Days of Storage	Deproteinised Rubber				Rubber containing Casein			
	Laboratory Storage		Storage over Calcium Chloride		Laboratory Storage		Storage over Calcium Chloride	
	Raw Mooney Viscosity	Weight Change	Raw Mooney Viscosity	Weight Change	Raw Mooney Viscosity	Weight Change	Raw Mooney Viscosity	Weight Change
0	56½		56½		70½		70½	
1		-0.09%		-0.27%		+0.03%		-0.47%
2		-0.19%		-0.33%		+0.02%		-0.54%
3		-0.20%		-0.34%		+0.04%		-0.56%
5	53	-0.27%	78½	-0.36%	73	+0.14%	88	-0.59%
6		-0.30%		-0.36%		Nil		-0.58%
9				-0.36%				-0.59%
10		-0.34%		-0.37%		-0.01%		-0.59%
13		-0.34%		-0.36%		-0.01%		-0.60%
15		-0.35%	81	-0.35%		-0.03%	90½	-0.60%
20		-0.36%		-0.35%		-0.06%		-0.61%
26	50½	-0.34%	76½	-0.34%	72	-0.06%	92	-0.61%

TABLE IV

Relative Humidity	10 Days Storage	30 Days Storage		92 Days Storage		183 Days Storage	
	Weight Change	Weight Change	Mooney Viscosity	Weight Change	Mooney Viscosity	Weight Change	Mooney Viscosity
0%	-0.35%	-0.36%	105.5	-0.34%	112.5	-0.33%	108.0
10%	-0.30%	-0.30%	88.0	-0.29%	95.0	-0.29%	93.5
32%	-0.20%	-0.20%	83.0	-0.20%	88.5	-0.20%	87.5
52%	-0.03%	-0.01%	81.0	-0.04%	85.5	-0.06%	83.5
79%	+0.37%	+0.42%	80.0	+0.47%	83.0	+0.38%	82.0
98%	+1.22%	+1.76%	79.0	+1.27%	82.5	+0.52%	81.0

Note.—Original Mooney Viscosity=77.5 units.

TABLE V

Days of Storage	Laboratory Storage			Storage over Calcium Chloride		
	Mooney Viscosity	Williams Plasticity (mm)	Williams Recovery (mm)	Mooney Viscosity	Williams Plasticity (mm)	Williams Recovery (mm)
0	77.0	4.00	5.02	77.0	4.00	5.02
4	77.0	3.99	5.85	79.0	4.09	5.90
10	77.5	4.35	5.60	84.0	4.43	6.58
15	78.0	4.10	5.88	88.0	4.45	6.51
20	79.0	4.32	6.05	88.0	4.57	6.90
35	80.0	4.39	6.11	98.0	5.15	9.40
60	80.5	4.32	6.37	103.0	5.96	11.35
90	82.5	4.18	5.94	105.0	5.63	11.30

TABLE VI

Laboratory-stored Raw Mooney 74.		Stored over Calcium Chloride Raw Mooney 103.	
Mooney after Breakdown		Mooney after Breakdown	
A.	B.	A.	B.
20.5	21.0	28.5	28.0
21.0	20.5	29.0	28.5
20.0	20.0	29.5	30.0

Mooney viscosity determinations were carried out on an N.B.S. model Mooney viscometer at 100°C using a large (1½ inches dia.) flat cross-hatched rotor. Samples were allowed to warm up for one minute in the instrument and readings were recorded after four minutes shearing. The Standard Error of testing for a single Mooney determination was 0.7 units. The Mooney values recorded in Tables I, III, IV and V are the means of duplicate determinations on different test portions taken from the same sample.

Plasticity and recovery values were determined using a Williams parallel plate plastimeter operating at 100° C. Plasticity numbers were recorded on spheres of 2 c.c. capacity after ten minutes of application of the load. Recovery was measured after ten minutes recovery at 100° C followed by fifteen minutes cooling at room temperature. The values recorded in Table V are the means of duplicate determinations on different portions from the same sample, and the Standard Error of testing for a single determination was 0.06 mm. for Plasticity and 0.09 mm. for Recovery.

Storage of samples was carried out in glass containers, the samples being in the form of sheets of approximately 25 gram weight, and of varying thicknesses depending on the experimental conditions. Controls were stored in the laboratory under tropical conditions (temperature $30 \pm 3^\circ \text{C}$; relative humidity 75 per cent ± 15 per cent), but in the absence of direct sunlight. For experiments at higher temperatures samples were stored in containers in electric, thermostatically controlled, air convection ovens.

Weight change data were obtained from separate portions of the samples under investigation, of weight approximately 5 grams, and all changes in weight are based on the original weight of the samples under investigation. The Standard Error of a single weight change determination was 0.01%.

Acetone-extracted samples were prepared by continuous extraction with cold acetone under nitrogen for twelve hours.

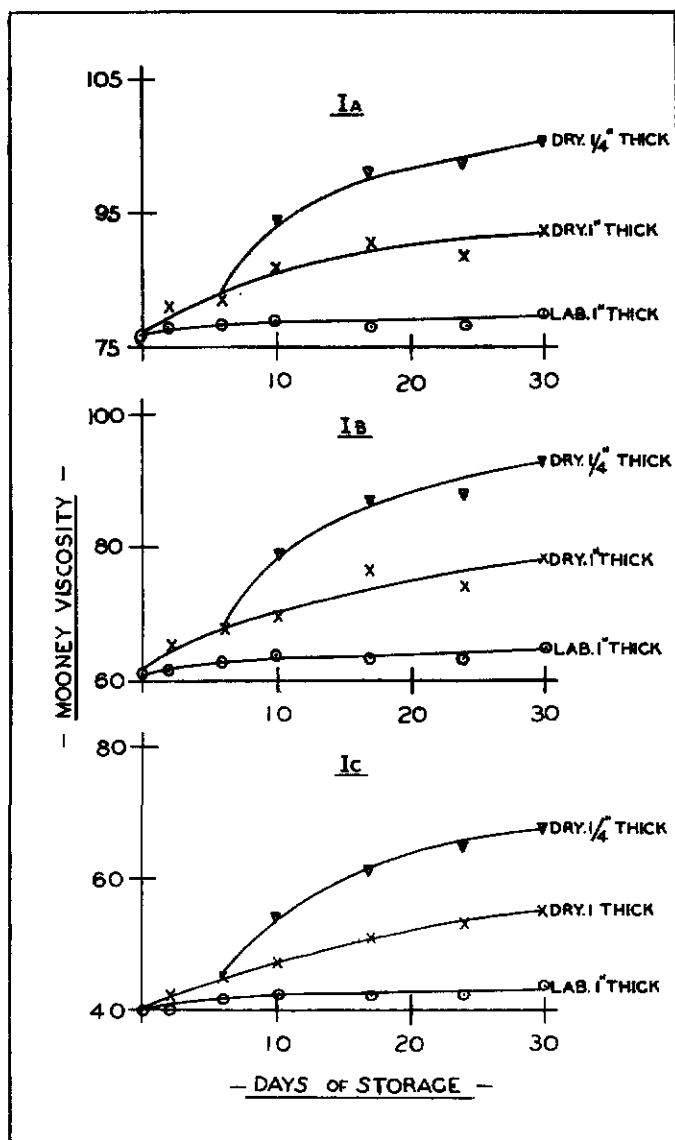
Deproteinised rubber was produced by multiple creaming of fresh latex with ammonium alginate, in the presence of ammonium oleate.

Experimental Procedure and Results

(1) Storage at Low Relative Humidity

(a) INFLUENCE OF SAMPLE THICKNESS

Since the extent of drying-out of a thick sample of rubber would be less than for a thinner sample under similar conditions, it appeared likely that specimen thickness would also influence the extent of the increase in hardness during storage at low relative humidity. To examine this, portions of a sample of R.S.S. were broken down by cold milling to give two levels of Mooney viscosity, and the unmasticated rubber and the two masticated samples were stored in approximately 1 inch thick slabs over calcium chloride at room temperature, with controls of the same thickness stored in the laboratory. After six days storage portions from the samples kept over calcium chloride were sheeted out to approximately ¼ inch thickness and storage continued. Samples were removed at intervals throughout the storage period and Mooney viscosity determinations carried out immediately after removal.

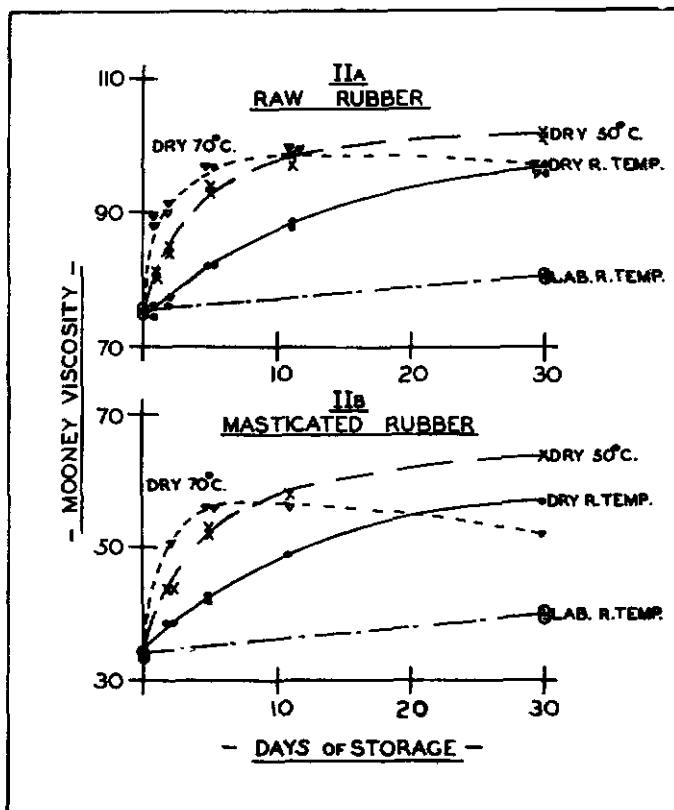


The results plotted in Figure I confirm that a greater increase of Mooney viscosity takes place on dry air storage than on storage under tropical conditions and that, as anticipated, the thinner samples harden more rapidly than the thicker. In these respects both unmasticated and masticated rubbers behave in a closely similar manner, which indicates that the changes are not restricted to a particular range of molecular weight.

(b) EFFECT OF TEMPERATURE OF STORAGE

A further obvious factor likely to influence the changes under investigation was temperature of storage. Portions of unmasticated and masticated R.S.S. rubber approximately 1/8 inch thick were therefore stored over calcium chloride at room temperature (ca. 30° C) and at 50° C and 70° C. Mooney viscosity changes

during a month of storage are shown graphically in Figure II. In the early stages the higher the temperature the greater the Mooney

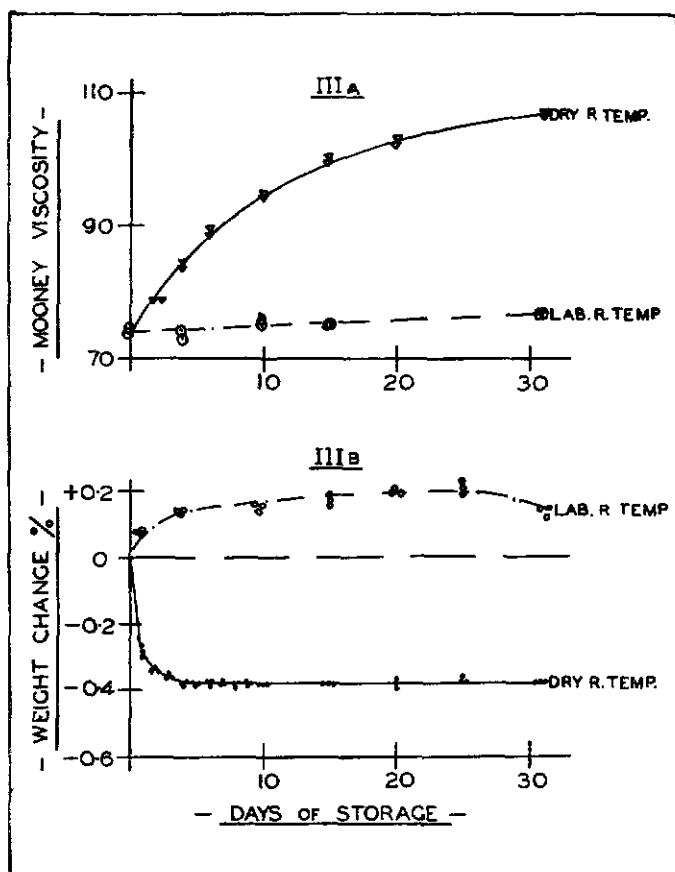


increase, but oxidative breakdown is apparent on prolonged storage at 70° C, and masks the hardening effect.

(c) RELATIONSHIP BETWEEN MOONEY VISCOSITY CHANGES AND WEIGHT CHANGES

In view of the large increase in Mooney viscosity of fresh natural rubber on storage at low relative humidity it was of interest to examine the possible relationship between the Mooney change and the moisture content of rubber. The long period during which the Mooney changes take place, as compared with the comparatively short time necessary to dry rubber in an oven, when no marked change in viscosity is apparent, suggested that Mooney changes would continue for a considerable time after constant weight had been reached during drying.

This was confirmed by the results of an experiment where both Mooney viscosity and weight changes were determined at intervals on approximately 1/8 inch thick samples stored over calcium chloride at room temperature. Control samples stored under tropical conditions were also similarly tested, and in addition data were recorded on the further changes in weight brought about by oven-drying to constant weight at 85° C for both the dry-air and tropical-stored samples. Test results are recorded in Table I and the Mooney viscosity and weight changes for room-temperature drying are shown graphically in Figure III.



The rubber reaches constant weight over calcium chloride after about five days, but slow Mooney increase is still taking place after thirty days of storage. Since the viscosity changes are apparent from the onset of drying, it is also evident that the rubber does not need to be completely dry before changes can commence.

It is of interest to observe that approximately 0.1 per cent of additional moisture and/or volatile matter is removed by heating the rubber at 85° C after it has reached equilibrium over calcium chloride at room temperature. In addition the use of a number of different drying agents indicated that the changes observed were brought about by the removal of moisture and were not dependent on the nature of any particular desiccant.

(d) PURIFIED RUBBERS

In considering factors responsible for hardening during low humidity storage attention was first directed to the non-rubber constituents. Acetone-extraction of natural rubber results in an immediate increase in Mooney value, presumably due to the removal of acetone-soluble materials which act as softeners, but from the data presented in Table II it can be seen that subsequent drying over calcium chloride produces a further increase which is considerably in excess of that which takes place during storage at high humidity.

TABLE II

Days of Storage	Raw Mooney Viscosity			
	Normal Rubber		Acetone-extracted Rubber	
	Laboratory Storage	Storage over Calcium Chloride	Laboratory Storage	Storage over Calcium Chloride
0	94	95	101	101
1	—	95½	—	102
4	95	98½	102½	104½
6	94½	102½	103	105½
10	95	104	103½	109
14	97	109	105½	112½
21	95	107	104½	112½
29	95½	108	105	114

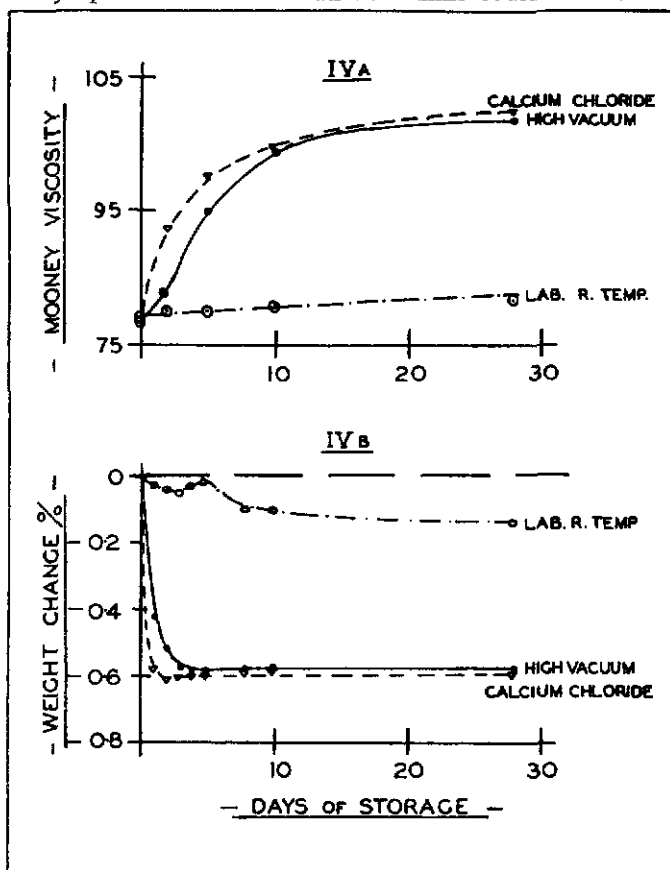
The close connection known to exist between the moisture content, rate of drying, and protein content of natural rubber suggested that the changes might be associated with hardening of the nitrogenous non-rubber constituents, and an examination was made of a deproteinised rubber, containing only a very small quantity of residual nitrogen. This material was prepared by repeated creaming of fresh field latex, to which ammonium oleate had been added, using 0.15 per cent ammonium alginate as a creaming agent. The resultant purified cream was divided into two portions and to one was added a solution of casein in ammonia water to give approximately 0.5 per cent casein on the dry rubber. Both latices were coagulated with acetic acid, creped out to approximately 1/8 inch thickness, and allowed to dry in the dark at room temperature. The rate of drying of the rubber containing added casein was noticeably more rapid than that of the purified material; the latter took over three weeks to become translucent and even then it was necessary to break up patches of very wet material by sheeting out at tight nip. The total nitrogen content of the deproteinised rubber was very low, being 0.028 per cent; the rubber containing casein had a total nitrogen content of 0.480 per cent.

Details of Mooney viscosity and weight changes on storage of these materials at low and high humidity are given in Table III. It is evident that the deproteinised rubber had not reached equilibrium with the laboratory conditions at the commencement of the experiment, since loss of weight continued throughout the storage period in the laboratory. Although it is unlikely that there would have been much marked difference in the final moisture content of the deproteinised samples after dry-air and

laboratory storage, storage at low humidity still gave a considerable increase in Mooney viscosity, and the behaviour in this respect was very similar to that of the samples containing deliberately added casein, and also of samples of normal smoked sheet. Similar conclusions are arrived at for storage of portions of the materials used in the above experiment after acetone extraction. In the case of acetone-extracted deproteinised rubber considerable oxidative breakdown is also apparent during storage, but the main effect of greater hardening at low humidity is not masked, and it is concluded that the major portion of the nitrogenous and acetone-soluble non-rubber constituents of Hevea rubber are not responsible for the hardness changes brought about by drying.

(e) HIGH VACUUM DRYING

Since non-rubber constituents did not appear to play any part in storage hardening, the function of the rubber hydrocarbon itself was next considered. It seemed possible that either atmospheric oxygen or oxygen dissolved in the rubber might be responsible for continued linear polymerisation or alternatively the build-up of cross links, these reactions being accelerated in the absence of moisture. Samples were evacuated on an all-glass high vacuum line using a rotary oil pump backed by a single stage mercury diffusion pump. Continuous pumping was carried out for periods of not less than five hours each day, the samples being sealed off from the line between each evacuation, and after about three days pressures of less than 10^{-4} mms could be maintained.

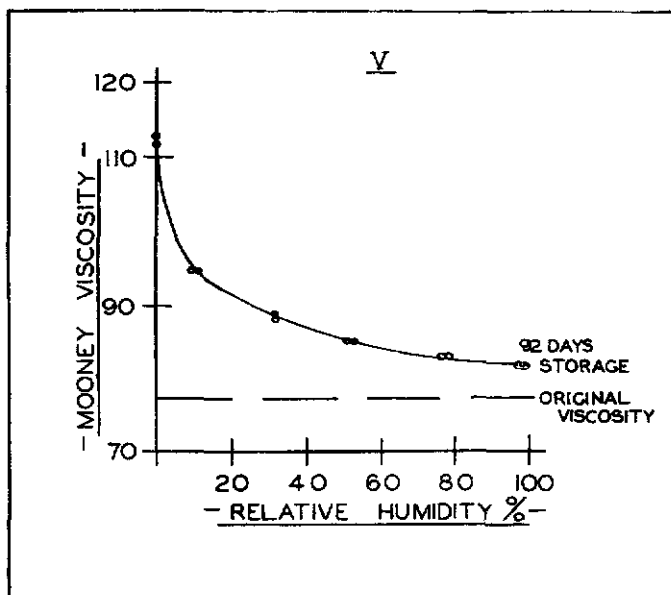


The results of experiments (Figure IV) show that although there is a lag both in Mooney increase and weight change during the early stages of vacuum drying, as compared with drying over calcium chloride (due in all probability to the intermittent nature of the former process in this experiment as compared with the continuous removal of moisture over a desiccant), corresponding values for both treatments are of the same order after about ten days storage. In consequence it is considered that oxygen is not directly involved in the mechanism.

(2) Storage at Different Relative Humidities

Since the Mooney viscosity of natural rubber did not appear to bear any close relationship to moisture content at any particular instant, it appeared that more valuable comparisons would be those showing hardening after prolonged storage at different relative humidities.

Mooney viscosity and weight change data obtained at intervals throughout a six-months period, for samples stored at 22° C between 0 per cent R.H. and 98 per cent R.H. are shown in Table IV. Figure V is a plot of Mooney viscosity against relative humidity after three months storage, when Mooney equilibrium



has been reached for these particular conditions with samples of approximately 1/8 inch thick. It is evident that the relative humidity of storage influences both the rate and the extent of the Mooney increase, and that increases are most marked when storage takes place below about 30 per cent R.H.

Weight change data at the higher humidities became unreliable after about thirty days of storage, due to development of mould growth.

(3) Alternate Storage at Low and High Humidity

In considering the practical consequences of the hardening of natural rubber, as demonstrated in the above experiments, it was

necessary to know whether a permanent change was produced, or whether the effect of low humidity storage could be reversed in whole or part by subsequent storage at high humidity.

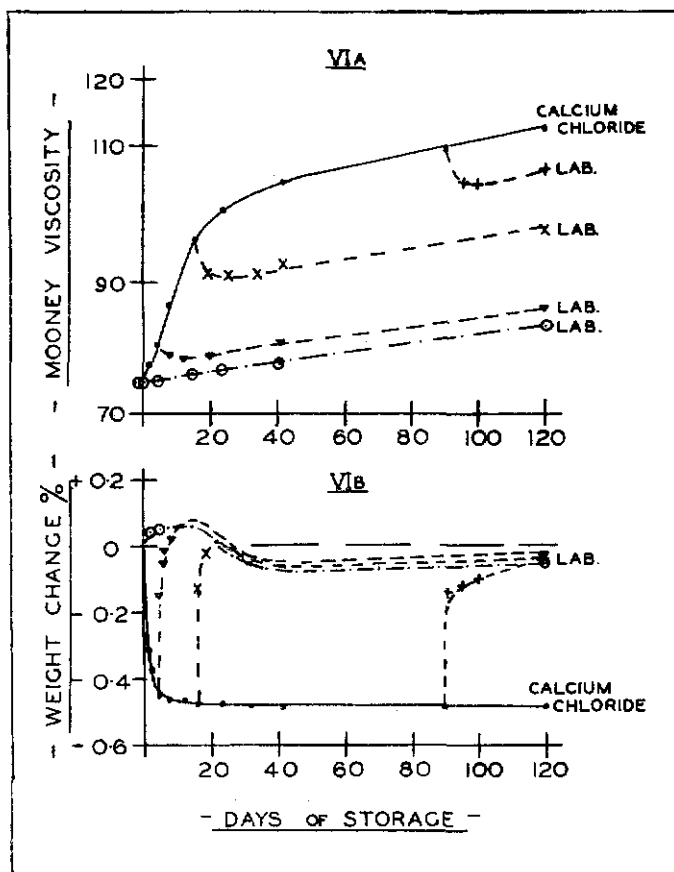


Figure VI illustrates the effect on Mooney viscosity and weight change of the return of approximately 1/8 inch thick samples to tropical conditions at intervals throughout a four-months storage period over calcium chloride at room temperature.

It is evident that only a small portion of the Mooney increase which takes place at low relative humidity can be reversed by further storage under tropical conditions, but despite the large differences shown up by Mooney values, different conditions of storage prior to reaching equilibrium in the laboratory have no significant effect on the final moisture content.

(4) Evidence for the Build-up of a Cross-linked Structure

In the course of these investigations it was noted that there was a marked difference in the behaviour of laboratory and dry-air stored rubbers on immersion in benzene. The former passed completely into solution as far as could be determined visually after three days at room temperature without agitation, whereas

the latter gave a macro gel structure with the swollen outline of the original sample shape still readily discernible after more than a week's immersion.

Attempts to apply the "Harris Cage" technique (7) of gel determination to obtain quantitative estimations of these changes in structure were not particularly successful, because of the high errors of reproducibility which were encountered. However, the method supplied a very definite qualitative indication of gel development, since laboratory-stored materials gave benzene-insoluble values in the range 2.5 per cent to 6 per cent, whereas low-humidity-stored samples ranged from 25 per cent to 54 per cent.

Comparisons of Mooney viscosity and Williams plasticity values respectively, under conditions of high and low humidity, confirmed the findings of the earlier investigations with regard to increases in hardness as measured by the parallel plate instrument during dry storage, but in addition very large increases in the "recovery" values were also observed under these conditions.

Table V gives Mooney and Williams data on samples stored wet and dry at room temperature for a period of three months. The rubber was in the form of 1 inch thick mill-blended slabs to allow cutting of the plasticity test pieces without the need for milling which might have resulted in some break-down of structure. The increase in the recovery value of 125 per cent for the samples stored over calcium chloride as compared with the increase of only 18 per cent for laboratory-stored material suggests the development of a lightly cross-linked structure with a consequent increase in "nerve" during storage of rubber in the absence of moisture.

(5) Technological Properties

As mentioned earlier it is evident that by the time natural rubber reaches the consumer changes have already taken place to a lesser or greater extent, depending on the time and conditions of storage, and "fresh" rubber would never be available to a manufacturer unless his factory was situated in a rubber-producing area. It was nevertheless of interest to compare the technological behaviour of fresh rubber and storage-hardened rubber from the same latex source. The "stored" rubber for this experiment was prepared by rapid drying of a portion of a mill-blended sample of R.S.S. 1 at 50° C over calcium chloride for seven days, followed by six days storage under tropical conditions, and this was compared with the remaining portion of the blended sample kept in the laboratory throughout the storage period. Such a comparison is not strictly the same as between a fresh rubber and one which had been stored for a long period during transit from producer to consumer, since slow changes other than those associated with drying-out may take place, and these in all probability contribute to the final characteristics of the rubber. However, from the point of view of investigating effects due to hardness changes on drying, the treatment given seemed likely to establish whether any major technological changes could be attributed to this source.

TABLE VII

Rubber	Raw Mooney Viscosity	Mixing Cycle mins	Compound Mooney Viscosity	Press-cured at 140° C											
				Tensile Strength Kg/Sq. cm.			Elongation at Break			Modulus at 600% (M.C.) Kg/Sq. cm.			Resilience at 70°C		
				20'	40'	80'	20'	40'	80'	20'	40'	80'	20'	40'	80'
Laboratory-stored	74	2½	42	92	120	121	870%	870%	873%	29	37	37	69.3%	73.6%	72.6%
Stored over Calcium Chloride	103	2½	55	124	132	116	851%	836%	820%	44	51	48	72.6%	76.8%	74.2%
		4	44½	119	133	129	887%	866%	860%	34	42	41	73.2%	74.9%	75.7%

TABLE VIII

Period of Drying Days	Mooney Viscosity	
	Smoked Sheet	Air-dried Sheet
3	Not dry	73
4	70	76½
5	71	77½
6	70	78½
7	71	78½

Comparison of relative rates of breakdown were made by subjecting 50-gram portions to twenty-five straight-through passes on a cold laboratory mill at friction ratio, and tight nip, with rolling and up-ending between each pass.

Results given in Table VI indicate that the rate of breakdown of the hardened rubber, as measured by change in Mooney viscosity, is greater than for the normal fresh material, but that after a similar breakdown schedule the latter is still appreciably softer.

This effect is further confirmed when examining behaviour during compounding in the A.C.S. 1 pure gum test mix. After a two-and-a-half-minute mixing schedule on a laboratory mill, the normal rubber gave a compound viscosity of 42 Mooney units, while for a similar schedule the hardened rubber gave a compound viscosity of 56 Mooney units. Increase of mixing time to four minutes gave a compound viscosity of 44½ units for the latter material.

Comparisons of vulcanised properties for the fresh rubber, and for the hardened rubber at the two levels of breakdown described above, are set out in Table VII.

It is evident that even after the additional breakdown required to bring the compound stock viscosity of the dried rubber close to that of the control, the former is showing an improvement in *general technological properties for a pure gum mix*, and it seems evident that the structure built up during drying still persists after breakdown and compounding. It is unlikely, however, that improvements of this order, which are associated with hardness changes close to the maximum obtainable during drying, will prove of much practical significance to the manufacturer.

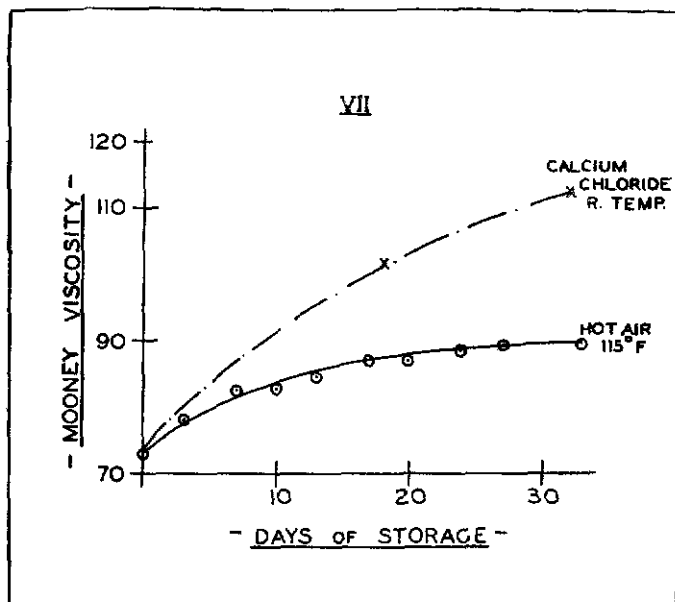
(6) Effect of Drying Conditions during Preparation

The dependence of the level of the Mooney viscosity of natural rubber on the extent of drying during storage suggested that variation in the time and conditions of sheet drying during preparation could result in different hardness levels for fresh rubber prepared from the same latex source.

To confirm this smoked sheets and air-dried sheets were prepared by normal estate factory procedures from the same bulk of latex. In each case samples were taken for Mooney testing as soon as the rubber appeared dry as judged by the production of a translucent sheet, and in addition sampling was carried out at intervals during continued drying.

Results are given in Table VIII, from which it is evident that increasing the drying time in the smokehouse has had no appreciable effect on the level of Mooney viscosity, presumably because both Mooney and moisture equilibrium had been reached by the time the sheet appears translucent. With the hot air-dried material, however, the rubber became translucent before arrival at equilibrium with respect to Mooney viscosity and moisture content, and consequently increased drying time resulted in an increase in Mooney viscosity.

After removal from the estate factory drying sheds, continued drying of these samples was carried out in a laboratory hot-air chamber at 115° F, and also over calcium chloride at room temperature. All samples exhibited very similar behaviour and Figure VII illustrates a typical set of results.



Continued drying under different conditions of temperature and humidity results in a new and higher level of viscosity being reached; in this particular experiment the values after prolonged drying at 115° F were still considerably lower than corresponding values for storage over calcium chloride.

Conclusions and Discussion

The main conclusions reached as a result of the investigations reported above may be summarised as follows:

(a) The relative humidity of the surrounding atmosphere has a marked influence on the increase in hardness of natural rubber during storage. Both raw and masticated rubbers behave in a similar manner in this respect.

(b) Increases in Mooney viscosity continue for a considerable time after the rubber has reached constant weight during drying.

(c) At a fixed temperature the highest Mooney viscosity value is reached at the lowest relative humidity, and in addition the time taken to reach this value is shorter the lower the humidity.

(d) Increases are most marked in the region below about 30 per cent R.H. At zero humidity the rate of change and in all probability the extent of the increase is greater the higher the temperature in the range examined (30° C to 70° C). However, during storage in dry air oxidative breakdown becomes excessive and masks the hardening effect when temperatures are increased and storage is prolonged.

(e) The hardening is only partially reversed by subsequent storage at high humidity. At room temperature the changes are unaffected by the absence of oxygen or by the removal of acetone-soluble and nitrogenous non-rubber constituents, and are evidently associated with the rubber hydrocarbon itself.

(f) Evidence of the formation of a benzene-insoluble gel and the development of abnormally high Williams recovery values suggests the build-up of a cross-linked structure throughout the rubber.

(g) This structure influences the breakdown characteristics of the raw rubber during mastication and shows up in the slightly improved technical properties of vulcanised pure gum products, persisting even after additional breakdown has been given to arrive at "normal" levels of compound stock viscosity.

(h) Changes in the conditions of sheet drying in an estate factory can result in different raw Mooney viscosity values for freshly-prepared rubber from the same latex source. Heterogeneous humidity conditions within commercial smokehouses and drying sheds and different conditions from day to day may well account for a proportion of the variability in hardness observed with raw natural rubber.

The work described above was carried out to obtain information on storage changes, and the results are recorded primarily to cover this particular requirement. However, it is of interest to consider briefly the possible mechanisms which may be involved in the phenomena observed.

The evidence points to the rubber hydrocarbon as the main participant, and over a wide range of initial molecular weights the effects were very similar.

The hardening which takes place as a result of drying appears to be due to an increase in the number of molecular linkages present. Development of high recovery and the formation of a macrogel structure suggests that these are cross-links between chains rather than a coupling of existing units to produce longer or more highly-branched molecules.

In this connection Medalia and Kolthoff (7) have recently reported a method for the conversion of microgel to macrogel in GR-S which involves heating in a vacuum oven at 80° C under a pressure of 20 to 40 mm. of mercury for twelve hours. Since drying-out must occur under these conditions the changes with GR-S may be closely related to those observed in the present work with natural rubber.

It seems probable that the overall effects are the result of two opposed processes, one the normal oxidative breakdown, and the other a molecular build-up which may be initiated and maintained by the presence in the fresh rubber of peroxide or similar free radical forming groups.

Under conditions of tropical storage at high relative humidity the balance for a freshly-prepared rubber is very slightly in favour of structure build-up and a slow increase in hardness takes place until equilibrium is reached. Removal of water during storage at lower humidities upsets the balance between the opposed processes to give increased structure build-up, and the new equilibrium position is to a large extent maintained when storage is continued after return to conditions of tropical humidity.

Recent observations which still await confirmation indicate that addition to rubber of mercaptobenzothiazole or xylyl mercaptan considerably reduces the hardening during storage in

dry air. Substances of this type increase the effect of oxidative breakdown during the mastication of rubber and may be reacting in a similar manner in this instance.

The effect of water in shifting the equilibrium between build-up and breakdown could be accounted for in one of two ways—either as an accelerator of oxidative breakdown or as a retarder of molecular build-up. The answer to the question as to which of these roles predominates should provide valuable insight into the nature of these changes, and may well indicate the steps which can be taken to control them.

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