

Creep of 'Pure-Gum' Vulcanisates of Natural Rubber

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The creep of vulcanisates of natural rubber cured with varying amounts of dicumyl peroxide was compared with that of vulcanisates cured by typical conventional sulphur-accelerator systems. The measurements involved indentation of a flat rubber disc as a function of time t and temperature T . The product of shear compliance J and T as a function of $\log t$ was represented by a family of curves with T as the parameter. For the vulcanisates cured with the sulphur-accelerator system, previous work has shown that the individual curves could be shifted along the abscissa to yield a single continuous curve with a slope which increased from a negligible value to a maximum and then decreased, continuing through a region of minimum slope which extended over about 7 decades of time before ending in a region of increasing slope. The value of the creep was 1.5-2.0% per decade in the region of minimum slope.

When the same procedures were applied to the vulcanisates cured with dicumyl peroxide, the individual curves of JT against $\log t$ at each temperature did not yield a single continuous curve when shifted. In a limited region just above the glass transition temperature, the creep was appreciable, but neither a constant-activation-energy shift nor a Williams-Landel-Ferry shift was satisfactory. Above this region it was clearly impossible to obtain a single curve, since the compliance-temperature product at a given time increased with increasing temperature while the corresponding creep of the dicumyl peroxide vulcanisates was generally too small ($<0.5\%$ per decade) to be measured between 5 and 600 seconds, except when the compound contained less than 2.5 parts of effective dicumyl peroxide. Outside of these regions the shear modulus was found to increase linearly with temperature. The investigation included temperatures as high as 100°C and effective dicumyl peroxide concentrations as high as 25 parts per hundred of rubber. The present results for the modulus and creep of dicumyl peroxide systems show good agreement with the published data of Chasset and Thirion (obtained by stress relaxation at 30°C) and of Plazek (obtained by a torsion pendulum) over the ranges they investigated.

The creep of vulcanisates of natural rubber cured with conventional sulphur-accelerator combinations has been studied in two previous investigations at the National Bureau of Standards. In the first (WOOD AND ROTH, 1963), described in a paper presented at the International Rubber Technology Conference in London in 1962, data were given for compounds containing two different accelerators (mercaptobenzothiazole and dibenzothiazyl disulphide). In the second, data were obtained (ROTH *et al.*, 1965) for varying times of cure over a range of temperature from that at which rubber-like compliance is first observed

to that at which degradation becomes appreciable during the time of the experiment. The present work compares the results obtained in those studies with the corresponding values obtained in new experiments with vulcanisates cured with dicumyl peroxide in varying amounts.

Some similarities are noted but in other respects there are striking differences, corresponding to the differences in the nature of the cross-links formed. The present paper discusses the time-dependent effects, manifested as creep, while a later publication will deal with a discussion of the pseudo-equilibrium modulus.

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Creep, as observed experimentally, may be expected to arise from the viscoelastic phenomenon called delayed elasticity, strongly evident near the glass transition temperature, from irreversible flow, or from other causes. Flow is to be expected in a non-crosslinked system or one with a low degree of cross-linking. Flow can also arise from thermal degradation with consequent rupture of bonds. Degradation would be most pronounced at high temperatures and long times.

EXPERIMENTAL PROCEDURE

The vulcanisates studied in the present investigation were prepared by mixing natural rubber (*National Bureau of Standards—Standard Reference Material 385b*) with varying amounts of dicumyl peroxide, and curing for 120 minutes at 149°C to form disc specimens about 35 mm in diameter and 9 mm in thickness. The amounts p of dicumyl peroxide added to each 100 parts by weight of rubber were 0, 0.5, 1, 2, 3, 4, 5, 7, 8, 10, 15, 20, and 25 parts respectively. Larger amounts of dicumyl peroxide yielded specimens which were too brittle for satisfactory handling.

The results of Hummel and co-workers (HUMMEL *et al.*, 1961) would indicate that the half-life of dicumyl peroxide at 149° is about 25 minutes. Consequently it would be expected that, during the curing time of 120 minutes (4.8 half-lives), about 96.4% of the peroxide added should have been decomposed and thereby rendered effective for cross-linking.

The shear compliance J (defined as the limit of the ratio of strain to stress at zero deformation) was calculated for each specimen from observations of the indentation of the flat rubber surface by a rigid sphere. The instrument used conformed to the requirements of A.S.T.M. Method D 1415-56T for determining International Rubber Hardness (*I.S.O. Recommendation R48, 1957* and *British Standard BS 903 Part A7, 1957*). Details of the operation of the instrument and the calculation of the shear compliance are given in the two previous papers (WOOD AND ROTH, 1963; ROTH *et al.*, 1965).

In the present work a linear transducer was used to measure the displacement of a ball

indenter 2.38 mm in diameter as the load was increased from 30 to 564 g. A chamber surrounding the specimens was used to maintain any constant temperature in the range from -100° to $+100^{\circ}\text{C}$.

In order to eliminate effects arising from crystallisation of the rubber, only a few observations were made at temperatures in the range from -30° to $+20^{\circ}\text{C}$. Crystallisation might be especially pronounced at low degrees of cross-linking. Observations were normally made over the range of times from 5 to 600 seconds after the application of the load.

RESULTS (WITH CONVENTIONAL VULCANISATES)

Typical results obtained in this manner in the earlier work are shown in *Figure 1*, where the product of compliance J and temperature T in $^{\circ}\text{K}$ is plotted against the logarithm of the time at 12 different temperatures. The vulcanisate was made from the A.S.T.M. Recipe 1A, which uses mercaptobenzothiazole as the accelerator. It was cured 40 minutes at 140°C .

For pure-gum vulcanisates of natural rubber and the four chief synthetic rubbers it was

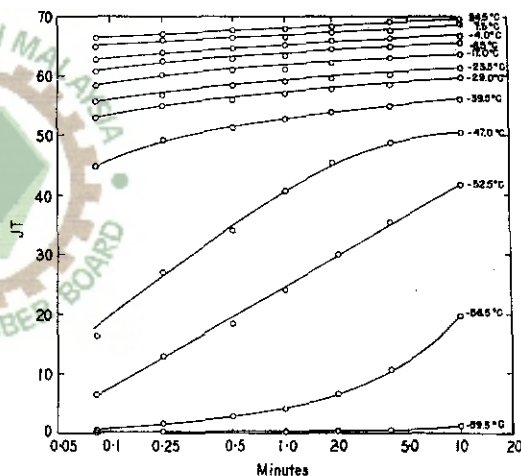


Figure 1. Product of compliance J ($\text{cm}^2 \text{Md}^{-1}$ or $10^{-5} \text{m}^2 \text{N}^{-1}$) and temperature T ($^{\circ}\text{K}$) plotted against $\log t$ (minutes) for several temperatures. Natural rubber vulcanisate A.S.T.M. 1A cured 40 minutes at 140°C .

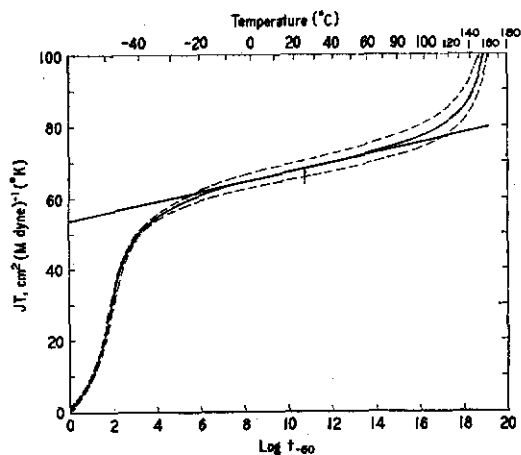


Figure 2. Product of compliance [$\text{cm}^2 (\text{Md})^{-1}$ or $10^{-5} \text{m}^2 \text{N}^{-1}$] and temperature ($^{\circ}\text{K}$) plotted against logarithm of equivalent time (in minutes) at -60°C . Natural rubber vulcanisate A.S.T.M. 1A cured 80 minutes at 140°C . Scale at top shows temperature at which 1-minute compliance-temperature product has value shown by graph. Arrow indicates 1-minute compliance-temperature product at 25°C .

found, in accordance with the observations of many previous workers, that the curves at different temperatures, as typified by Figure 1, could be shifted by different amounts along the log-time axis to yield a single sigmoid curve.

Typical results of such shifting are shown in Figure 2 where the A.S.T.M. 1A vulcanisate of natural rubber and sulphur accelerated with mercaptobenzothiazole cured for 80 minutes was investigated over a wide range of temperature. This figure, built up by the successive shifts just mentioned, illustrates the creep of a typical pure-gum vulcanisate over a range of almost 19 decades of equivalent time. The time-scale is given in terms of equivalent time at -60°C . The non-uniform scale of abscissas at the top of the graph shows the temperature at which the 1-minute compliance-temperature product has the value shown by the ordinate. The arrow indicates the 1-minute compliance-temperature product at 25°C .

The creep $dJ/d \log t$ is readily calculated from $dJT/d \log t$, the slope of the curve in Figures 1 and 2. The value of the latter quan-

tity increases from negligible values below the glass transition to reach a maximum, and then decreases to a minimum value which is maintained over a range of more than 7 decades. The 1-minute value at 25° occurs near the middle of the range. Finally at higher temperatures there is a region of increased slope, corresponding to the 'secondary creep' studied by GENT (1962).

In all the results for each vulcanisate mentioned thus far, the slope, $dJT/d \log t$, of the curve at a given value of JT was found to be the same within experimental uncertainty, whatever the temperature at which it was measured. Of course one would not have obtained a single curve by displacements along the log-time axis if this requirement had not been fulfilled.

When the magnitudes of the shifts necessary for the superposition of the different curves were plotted as a function of $1/T$, the results for unvulcanised natural rubber and for the two pure-gum vulcanisates of natural rubber were found to correspond to a constant activation energy. This behaviour is in contrast with the predictions of the equation of Williams, Landel and Ferry, which have been reported by several previous workers to be valid for similar vulcanisates. A discussion of this discrepancy is contained in a previous paper (ROTH *et al.*, 1965) with special consideration of the results of PAYNE (1958). Payne's results, obtained from measurements of the complex dynamic shear modulus, were similar to ours in most respects but differed in this particular case.

RESULTS (WITH DICUMYL PEROXIDE VULCANISATES)

Typical results obtained with vulcanisates cured with dicumyl peroxide are shown in Figure 3, which may be compared with Figure 1. The vulcanisate in this case contained three parts of dicumyl peroxide per hundred parts of rubber and was cured for 120 minutes at 149°C as already mentioned.

The temperature at which the compliance becomes perceptible with the measurement techniques employed here is about 9° lower than the corresponding temperature in

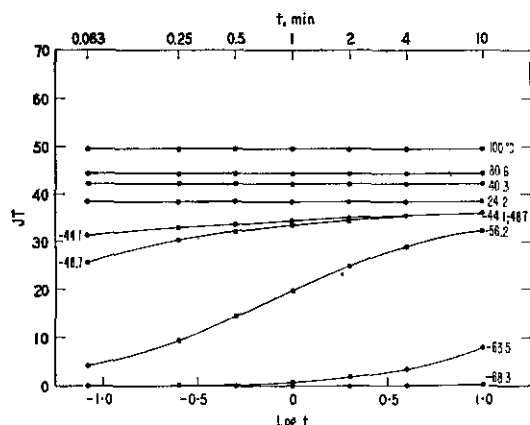


Figure 3. Product of compliance J ($\text{cm}^2 \text{Md}^{-1}$ or $10^{-5} \text{m}^2 \text{N}^{-1}$) and temperature T ($^{\circ}\text{K}$) plotted against $\log t$ (minutes) for several temperatures. Natural rubber 100 + dicumyl peroxide 3, cured 120 minutes at 149°C .

Figure 1. Thus it is concluded that the glass transition temperature T_g is not raised as much by dicumyl peroxide cross-linking as by the conventional sulphur-accelerator system.

The 1-minute compliance-temperature product for the dicumyl peroxide vulcanisate near 24° , on the other hand, is about $38 \text{ cm}^2(\text{Md})^{-1} (^{\circ}\text{K})$ or $38 \times 10^{-5} \text{ m}^2 \text{N}^{-1} (^{\circ}\text{K})$ as compared with 68 for the sulphur-accelerator system. These correspond to shear modulus values of 7.8 and 4.4 Md cm^{-2} (7.8 and $4.4 \times 10^5 \text{ Nm}^{-2}$) respectively. The increase of modulus on curing is thus seen to be considerably larger in the dicumyl peroxide system.

The creep $dJ/d \log t$, readily calculated from the slopes of the curves in Figure 3, is seen to be imperceptible at room temperature and above, but quite appreciable at -44° and lower temperatures. In general it was too small to be measured over the time range from 5 seconds to 10 minutes, a little more than two decades of time, unless the temperature was within a range of about 25° above the glass transition temperature or unless the dicumyl peroxide added was less than three parts per hundred of rubber.

When the creep was small it was difficult to determine how much to shift curves of the

type represented by Figures 1 and 3 to yield a single curve like those in Figure 2; when the creep was negligible, the task became impossible. Nevertheless, because this had been done successfully with the sulphur-accelerated vulcanisates, when the creep never was less than 1 per cent per decade, plots were made in which the curves were shifted by the amounts corresponding to an activation energy of about 37 kcal per mole, as found in the previous work, and also other plots corresponding to the predictions of the Williams, Landel and Ferry equation.

In the limited region just above the glass transition temperature the constant-activation-energy shifts appeared to be too small to represent those observed, while the Williams, Landel and Ferry shifts were too large. In this small region it might be possible to find some more satisfactory function than either of these. Over the whole range of higher temperatures, however, the compliance-temperature product at a fixed time always increased with increase of temperature but showed no perceptible change with time at a fixed temperature, except at low degrees of cross-linking. Under these conditions it will be obviously impossible to match any change in time by an equivalent change in temperature.

In summary it must be concluded that the change in the viscoelastic spectrum of dicumyl peroxide vulcanisates with time cannot be approximated over any appreciable range by an equivalent change in temperature. In this respect they differ from pure-gum vulcanisates cured with sulphur and conventional accelerators.

Figure 4 shows that the results obtained with the dicumyl peroxide vulcanisates may be represented by isochronal plots of shear creep modulus, $G=1/J$, against temperature. For convenience the lines are drawn to represent only the 10-minute moduli. The 5-second values, if different from the 10-minute values, are represented by a downward-pointing V. Except below -50°C (where the 5-second values are omitted to avoid confusion), the absence of a V means that no difference was noted between the 5-second and the 10-minute values of modulus.

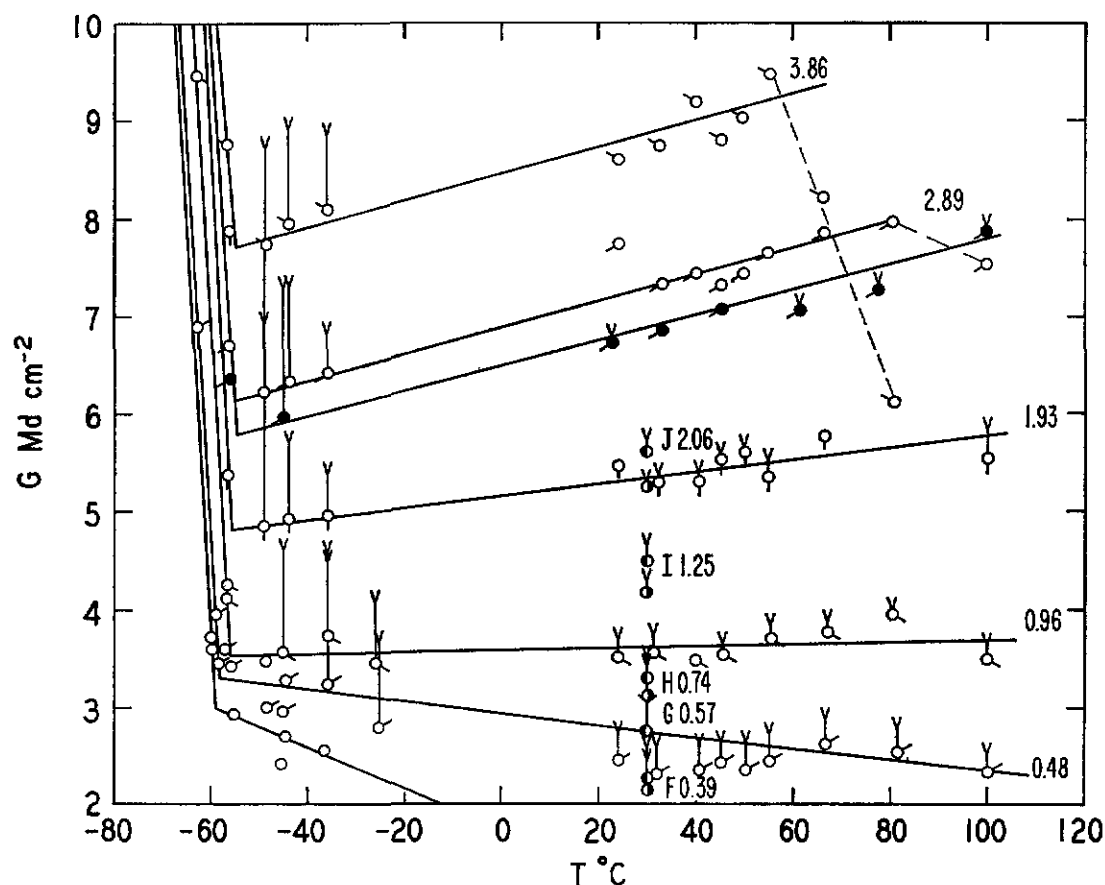


Figure 4. Shear modulus (Md cm^{-2} or 10^5 N m^{-2}) as a function of temperature. Natural rubber was cured with varying amounts of effective dicumyl peroxide. Numbers on graph give numbers of parts of effective dicumyl peroxide per hundred of rubber. ○ Open circles 10-minute moduli. ● Dark circles 10-minute moduli. Second set of observations with 2.89 parts of effective dicumyl peroxide. ◐ Left-shaded circles 10-minute moduli obtained from observations of CHASSET AND THIRION (1965). Specimens F, G, H, I and J. ◑ Right-shaded circles 10-minute moduli obtained from observations of PLAZEK (1966). Specimens F, H, I and J. Downward-pointing V's (V) indicate 5-second moduli where different from 10-minute values.

This type of plot, introduced by Meyer and Ferri and investigated in more detail by WITTE AND ANTHONY (1951) demonstrates clearly the drastic effect of the glass transition on modulus and creep, and illustrates the linear increase of modulus of a cross-linked rubber with temperature predicted by the kinetic theory of rubber elasticity. As noted by Witte and Anthony, there are pronounced time-effects in the neighbourhood of the glass transition at

all degrees of cross-linking. However, for temperatures 40° or more above the glass transition temperature, the creep decreased with increase of cross-linking, reaching a value of the order of half a per cent per decade for vulcanisates cured with 3 parts of dicumyl peroxide. This is about the minimum measurable with our experimental arrangement. For vulcanisates cured with larger amounts—from 4 to 25 parts—no creep whatever was noted.

It will be seen that for a given vulcanisate in the region from 20° to 100°C there is very little change of creep with temperature and specifically no great enhancement of creep up to 100°. With the exception of two anomalous results (shown by the dashed lines) there is likewise at 100° no noticeable reduction of modulus arising from degradation.

COMPARISON WITH PREVIOUS RESULTS

The results obtained with the dicumyl peroxide vulcanisates may be compared with those in two previous studies in other laboratories, utilising different methods of measuring the modulus and creep. In the first of these, CHASSET AND THIRION (1965) measured the stress relaxation at 30°C of vulcanisates maintained at 50 per cent elongation. This work shows the rate of stress relaxation, and consequently the creep, decreasing with increasing time over four decades. Our work with the indentation measurement extending over only about two decades was not precise enough to verify this observation, but was not in disagreement with it.

Chasset and Thirion added 3.5 parts of dicumyl peroxide to 100 parts of rubber and

cured for varying times at 135°C to obtain five specimens denoted as F, G, H, I, and J. The results of Hummel (HUMMEL *et al.*, 1961) yield a half-life value of 117.5 minutes for the decomposition of dicumyl peroxide at 135°. Table 1 shows our calculations of the fraction f of peroxide decomposed during the cure, and the corresponding number of parts fp of dicumyl peroxide (per hundred parts of rubber) effective in the cure.

The results of measurements of compliance J by a torsion pendulum have been reported by PLAZEK (1966), who made use of dicumyl peroxide vulcanisates F, H, I, and J, furnished by Chasset and Thirion.

Table 1 shows the values of shear modulus G obtained from the stress values read from the graphs of Chasset and Thirion at times of 6 seconds and 600 seconds. This operation was facilitated by Dr. Thirion, who was kind enough to make available a report containing Figure 3 of their paper (CHASSET AND THIRION, 1965) on a greatly-enlarged scale. Thirion has developed an equation which shows that the stress (or modulus) at infinite time would fall below the 600-second values shown here by about 15,

TABLE 1. MODULUS AND CREEP DATA FOR RUBBER CURED WITH DICUMYL PEROXIDE

Specimen	Time of cure, min	f	fp	Chasset and Thirion			Plazek		
				G , Md cm^{-2} or 10^5Nm^{-2}		Creep, % per decade	G , Md cm^{-2} or 10^5Nm^{-2}		Creep, % per decade
				6 s	600 s		6 s	600 s	
F	20	0.111	0.39	2.63	2.27	7.4	2.46	2.15	6.8
G	30	0.163	0.57	3.07	2.90	5.2	—	—	—
H	40	0.210	0.74	3.54	3.31	3.4	3.33	3.11	3.4
I	75	0.357	1.25	4.69	4.50	2.1	4.32	4.19	1.5
J	150	0.587	2.06	5.75	5.61	1.2	5.35	5.26	0.9

9, 5, 2, and 1 per cent respectively for specimens F, G, H, I and J.

To obtain the modulus, the stress values measured at 50 per cent elongation were multiplied by the factor 1.093, which is given by the empirical equation of Martin, Roth and Stiehler (MARTIN *et al.*, 1956; WOOD, 1958) as the ratio of shear modulus to stress at 50 per cent elongation. The stress relaxation modulus thus obtained is not exactly the same as the creep modulus measured in the present work. However the difference between the two is small when the creep is small, and will be disregarded in the present circumstances.

The last three columns of Table 1 show the modulus values calculated as the reciprocals of Plazek's shear compliances J . Here also the values were read from a large-scale graph in a report kindly supplied by Dr. Plazek.

A comparison of all three sets of observations at 30°C can be made in Figure 4, where the modulus values of Chasset and Thirion as well as those of Plazek are shown at 30° with the graphs of our own results. The values of the modulus for a given value of fp , the number of parts of decomposed peroxide, agree quite well especially when it is considered that they were obtained by three widely-different techniques. The values of the creep as measured by the difference between the 5-second (or 6-second), and the 10-minute modulus are seen to be in excellent agreement with each other, decreasing with increasing cross-linking in each case.

In future work it would be desirable to extend our observations over several more decades of time to determine more accurately the decrease of creep with increasing cross-linking, and to determine whether it approaches zero or a small finite value at high degrees of cross-linking. Likewise, information on this topic could be obtained by extending the observations of Chasset and Thirion or Plazek to higher amounts of effective dicumyl peroxide in the range from 2 to 24 parts per hundred of rubber.

SUMMARY AND CONCLUSIONS

In summary, the creep of vulcanisates of natural rubber cured with 3 parts of effective

dicumyl peroxide was about half a per cent per decade and changed very little with temperature up to 100°C, except near the glass transition temperature. When larger amounts—from 4 to 25 parts—were used, the creep was less than this, and no change in indentation was noted from 5 seconds to 10 minutes. The change in the viscoelastic spectrum of dicumyl peroxide vulcanisates with time was small and could not be approximated over any appreciable range by an equivalent change in temperature.

We conclude that the network of cross-links formed by curing with dicumyl peroxide is much more stable than that formed with conventional sulphur-accelerator systems, where the creep is never less than about one per cent per decade, and where changes in the viscoelastic spectrum with time can be approximated by an equivalent change in temperature.

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DISCUSSION

Chairman: Dr. A. A. Watson

Dr. Wood informed Dr. P. Thirion that the range of amplitude deformations was up to 1/50 000 inch. Dr. Wood asked Dr. H.W. Greensmith and Dr. A.A. Watson if they had considered the Wallace International Hardness Tester in their investigation into test systems for rate of cure. Dr. Greensmith said they did, but it was doubtful whether a hardness tester would be as sensitive or as simple as the Wallace Plastimeter. A further point was that the latter instrument was commonly used by producers.