Contamination of Field Latex and Solid Rubber by Copper Fungicides

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Copper fungicides were applied to the trunk and foliage of mature trees and subsequent copper contamination of latex, cuplump, and tree lace was measured. Observations made on the relationships between copper content and plasticity retention index (PRI) showed that the latter tends to decrease as copper increases. Copper contamination of latex was slight, but unacceptable contamination (>8 p.p.m.) of cuplump and tree lace occurred sporadically during 3 months after spraying 5 lb copper per acre.

Bordeaux mixture is widely used in Malaysia to control pink disease (*Corticium salmonicolor* Berk. et Br.) in immature *Hevea* rubber (HILTON, 1958; RUBBER RESEARCH INSTITUTE OF MALAYA, 1965). Copper fungicides, including Bordeaux mixture, are far more extensively employed in India for the control of *Phytophthora* leaf fall (RAMAKRISHNAN, 1961). Care has to be exercised in the application of such fungicides to mature trees because copper, by increasing the susceptibility of raw rubber to oxidation, has a deleterious effect on its ageing and mastication characteristics, leading to poorer physical and chemical properties (VILLAIN, 1950; BATEMAN AND SEKHAR, 1966). The maximum permitted level of copper in all grades of natural rubber is 8 p.p.m. (RUBBER MANUFACTURERS ASSOCIATION, 1962). RISDON (1958) and HEINISCH *et al.* (1961a) found that the copper content of field latex and tree scrap increased after dusting trees with copper fungicides, and drew attention to the danger inherent in repeated applications. With the occurrence of *Phytophthora* leaf fall in Malaysia (CHEE *et al.*, 1967), it became necessary to know if the amount of copper likely to be applied to the foliage of mature trees for the control of this disease would result in unacceptable copper contamination, and the duration of any contamination. In addition, an assessment was needed of the minimum period which should elapse after applying Bordeaux mixture to trees suffering from pink disease, before opening them to tapping.

TRUNK SPRAYING

In an experiment designed to investigate copper contamination resulting from spraying 1% Bordeaux mixture (containing 1% copper sulphate) against pink disease, three levels of the mixture (2, 4 or 8 pints per tree) were applied to goups of five 15-year-old trees. (The amount needed for one application for the control of pink disease would have been about one pint per tree, containing approximately 1.5g copper). The fungicide was applied with a knapsack sprayer to a 2-foot length of the trunk at the main fork about 20 ft above ground. Two pints were applied at a time and the deposit allowed to dry before spraying the remainder. Five trees were similarly sprayed with water to act as a control. Rubber was collected for 5 weeks before and 17 weeks after the fungicide was applied. Daily rainfall was also recorded.

Latex, tree lace and cuplump from one week's collection of three S/2.d/2 tappings were separately blended, creped (subjecting them to minimum milling and washing), dried at 140°F and analysed for their copper content. Latex films, prepared by drying field latex, were blended during the creping process. The mean amounts of copper (p.p.m.) per weekly sample were averaged for various periods to give the results summarised in *Table 1*.

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TABLE 1. COPPER CONTENT (P.P.M.) OF RUBBER COLLECTED AFTER SPRAYING BORDEAUX MIXTURE TO FORKS OF MATURE TREES

(Data from weekly crop of 5 trees per treatment)

Period of tapping		Type of rubber	Bordeaux mixture per tree (pints) 0	2	4	8
Before spraying (Mean of 5 tappings)		L	2.2	2.0	2.3	1.8
		CL	1.5	1.2	1.3	1.9
		TL	1.3	1.1	1.2	1.5
Weeks after spraying	1	L	2.5	5.2	5.7	4.9
		CL	3.6	48.8	11.6	37.6
		TL	4.3	9.1	24.1	31.3
	2–3	L	2.7	3.0	3.4	3.2
		CL	1.9	5.5	5.8	12.4
		TL	2.5	8.5	7.3	14.1
	4–5	L	2.3	2.4	2.8	2.2
		CL	1.7	2.4	2.4	4.0
		TL	2.0	2.8	2.3	6.0
	6–8	L	2.4	1.8	2.4	1.9
		CL	2.0	1.5	3.0	2.3
		TL	1.7	2.3	2.5	5.6
	9–11	L	2.7	2.2	3.5	2.2
		CL	1.9	4.6	5.5	8.9
		TL	2.2	3.3	1.6	9.9
	12–14	L	2.4	2.3	3.4	3.0
		CL	2.0	2.9	3.3	8.2
		TL	1.7	2.6	2.2	4.8
	15–17	L	3.2	3.0	3.9	3.3
		CL	1.7	2.2	2.8	3.6
		TL	2.2	2.3	2.6	3.9

L latex
CL cuplump
TL tree lace

During the first week after spraying the copper content of the latex doubled, irrespective of the amount of fungicide used. After a further two weeks it was back to normal, and at no time did it exceed the permitted maximum. Contamination of tree lace and cuplump was more severe, and at the highest level of application sporadically exceeded the permitted maximum during the following 14 weeks. At the lower levels of 2 and 4 pints per tree the maximum was only exceeded during the first 3 weeks, and thereafter exceeded 5 p.p.m. on only one occasion. The excessively high level of copper in cuplump during the first week of tapping may be largely accounted for by spray liquid running into the tapping cups before cup lump from the first tapping after spraying was collected.

During the period of the experiment a total of 22 in. of rain fell on 49 days, but there was no direct correlation between rainfall and the copper content of the crop.

FOLIAGE SPRAYING

Two plots of eight 10-year-old trees (each plot approximately 1/20 acre) were sprayed with 1% Bordeaux mixture, and two more plots with a 0.5% solution of a proprietary copper oxychloride fungicide containing 50% copper, using a knapsack mistblower to cover as much of the foliage as possible. The application rate of copper for all four plots was equivalent to 1 lb per acre, or approximately 3g per tree. Tapping cups were inverted before spraying. The total collection of each type of rubber from each plot was separately blended and creped after every tapping, and copper analyses carried out, particularly on samples of low Plasticity Retention Index (PRI) calculated by a standard method (RUBBER RESEARCH INSTITUTE OF MALAYA, 1966). With only a few trees having been sprayed, the size of the rubber samples was insufficient, so the experiment was terminated after seven tappings. Results are summarised in *Table 2*.

PRI is a measure of the oxidisability of raw rubber (BATEMAN AND SEKHAR, 1966); a satisfactorily high PRI indicates that metallic contaminants which might cause oxidation are not present in sufficient quantity to do so. *Table 2* shows that the PRI of the latex films ($\geq$98) was satisfactory throughout the period of the experiment. Rainfall during the period (14 days) was 4.7 in. Latex of the first tapping was in fact collected before spraying, the cuplump and tree lace after; although inverting the cup during spraying avoided direct contamination of cuplump, the lace on the tree at the time was heavily contaminated by spray drift (*Table 2*). Contamination of cuplump (as indicated by the copper analyses and suggested by the depressed PRI) persisted for two further tap-

TABLE 2. EFFECT ON COPPER CONTENT AND PRI OF RUBBER OF SPRAYING COPPER FUNGICIDES TO THE FOLIAGE OF MATURE TREES
(Data from two plots per treatment)

Period of tapping		Type of rubber	Bordeaux		Copper oxychloride	
			PRI	Copper (p.p.m.)	PRI	Copper (p.p.m.)
Before spraying (Mean of 2 tappings)		L	105	1.0	114	1.0
		CL	–	1.0	–	1.2
		TL	46	1.4	43	1.6
Tappings after spraying	1	L	99	1.6	100	1.3
		CL	–	1.4	–	2.2
		TL	36	17.7	45	40.7
	2	L	103	–	109	–
		CL	56	3.1	25	13.6
		TL	35	5.5*	47	5.5*
	3	L	101	–	104	–
		CL	69	–	54	–
		TL	49	4.8*	48	4.8*
	4	L	103	–	109	–
		CL	95	–	92	–
		TL	78	1.7	68	2.0
	5	L	99	–	103	–
		CL	95	–	80	–
		TL	59	1.3	42	15.8
	6	L	99	–	103	–
		CL	–	–	100	–
		TL	41	1.7	–	3.1
	7	L	98	–	101	–
		CL	–	–	–	–
		TL	–	2.8	–	2.6

* Mean data from all four plots (both treatments)
L latex
CL cuplump
TL tree lace

pings. At the end of the experiment the copper content of tree lace in the Bordeaux mixture-sprayed plots was twice as high as the pre-treatment level, but it had exceeded the maximum at only one tapping. Considerably higher levels of copper were obtained from plots sprayed with the copper oxychloride formulation, and the maximum level was exceeded at two tappings. Bordeaux mixture, being more rain-resistant once it has dried, would be expected to release smaller amounts of copper but over a longer period.

A second foliage spraying was carried out at a higher level of application of copper (5 lb per acre or approximately 15g per tree) to two fresh ¼-acre plots—large enough to give sufficient samples for complete analysis. Copper was applied as formulated copper oxychloride; tapping cups were again inverted while spraying. PRI tests and copper analyses of the crop, carried out as before, continued for 40 tappings, including 3 pre-treatment tappings, spread over 12 weeks.

Contamination of Latex

The copper content of the first sample after spraying was not significantly higher than the pre-treatment level. Due to rain no latex was obtained from the second tapping; at the third the copper level in one plot was 5.7 p.p.m. (four times the pre-treatment level) and in the other 1.5 p.p.m. Thereafter the levels became normal. No further copper analyses were carried out after the sixth tapping, but the PRI, never below 88, indicated that no appreciable contamination occurred.

Contamination of Cuplump and Tree Lace

Due to heavy rainfall the first tapping after spraying yielded no cuplump or tree lace, but the maximum permitted copper level (8 p.p.m.) was exceeded in the cuplump from one or other of the plots on the 2nd, 3rd, 5th, 8th, 17th, 18th, 22nd, 29th, 30th, 33rd and 36th tappings. The highest level (20.9 p.p.m.) was obtained at the 36th (penultimate) post-treatment tapping. The maximum level was similarly exceeded in tree lace on the 2nd–6th, 14th, 31st, 33rd, and 35th–37th tappings. The mean figures of copper content from both plots are set out in *Figure 1*, which also shows the rainfall after each tapping before the collection of the solid rubber. No clear relationship can be seen between rainfall and copper content.

DISCUSSION

All three experiments indicate an unexpectedly low level of copper in latex after spraying with a copper fungicide, even at levels as high as 12 g copper per tree applied to the trunk. The

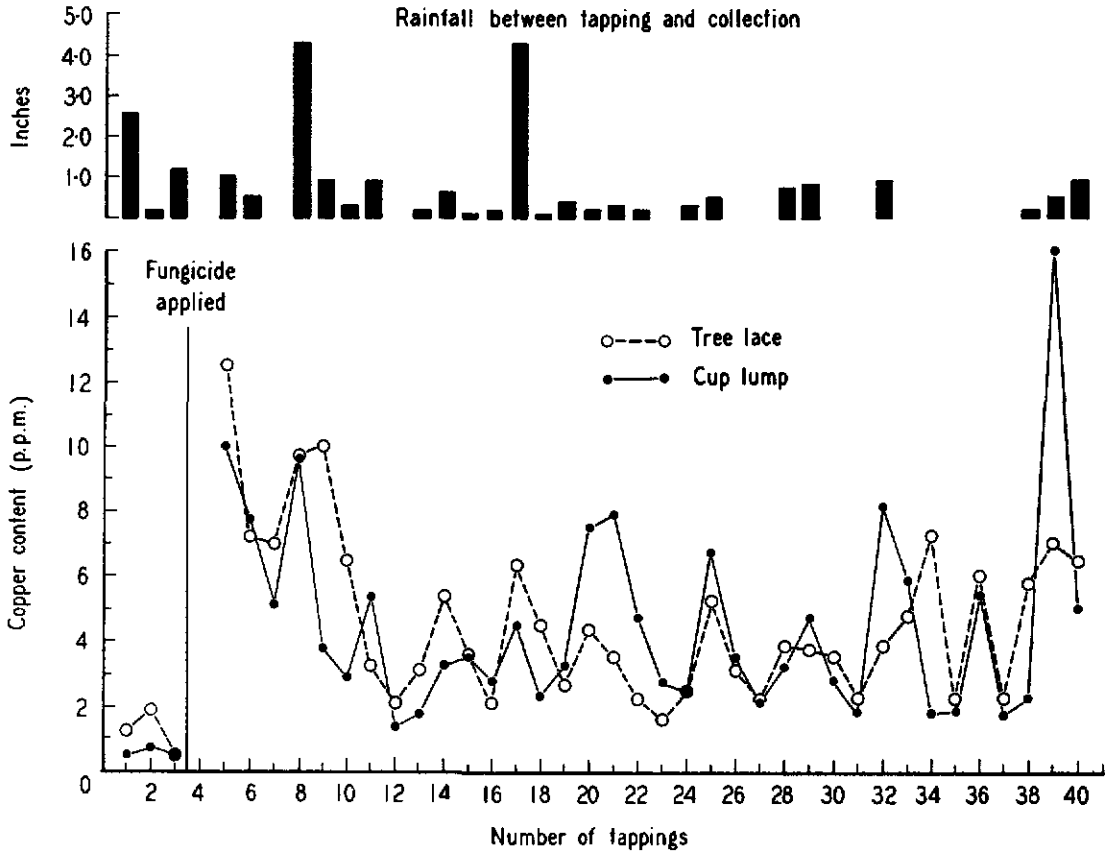

Figure 1. Rainfall (in.) and copper content (p.p.m.) of scrap rubber after each of 40 tappings following a copper fungicide application. Mean data from two plots.

persistence of copper in tree lace and cuplump, however, (for 14 weeks in the first experiment and 11½ weeks in the third) is noteworthy. It was found in Ceylon (HEINISCH *et al.*, 1961a) that contamination of rubber from treating the foliage of mature trees with copper dust occurred mainly in the scrap grades, and it was suggested that this was due to the absorption of copper by the leaves or roots leading to a higher content of phenol oxidase (a copper-containing enzyme) in the scrap, the enzyme being secreted from bark tissues wounded by tapping. It seems more likely that heavy contamination of scrap grades results from copper being washed down the trunk by rain to accumulate on the tapping cut and in the tapping cup, where it is adsorbed on the solid rubber. If copper is indeed absorbed by the leaves and assimilated by the tree as HEINISCH *et al.* suggested, this would account for the fact that in the present experiments the copper content of scrap was occasionally high even in dry weather. However, this suggestion does not explain why such dry weather contamination should occur only in the late drippings (cuplump) and not in latex.

Absence of latex contamination does not indicate that Bordeaux mixture can safely be used for the control of pink disease on trees in tapping, for the danger of contaminating scrap rubber remains, but the results indicate that a

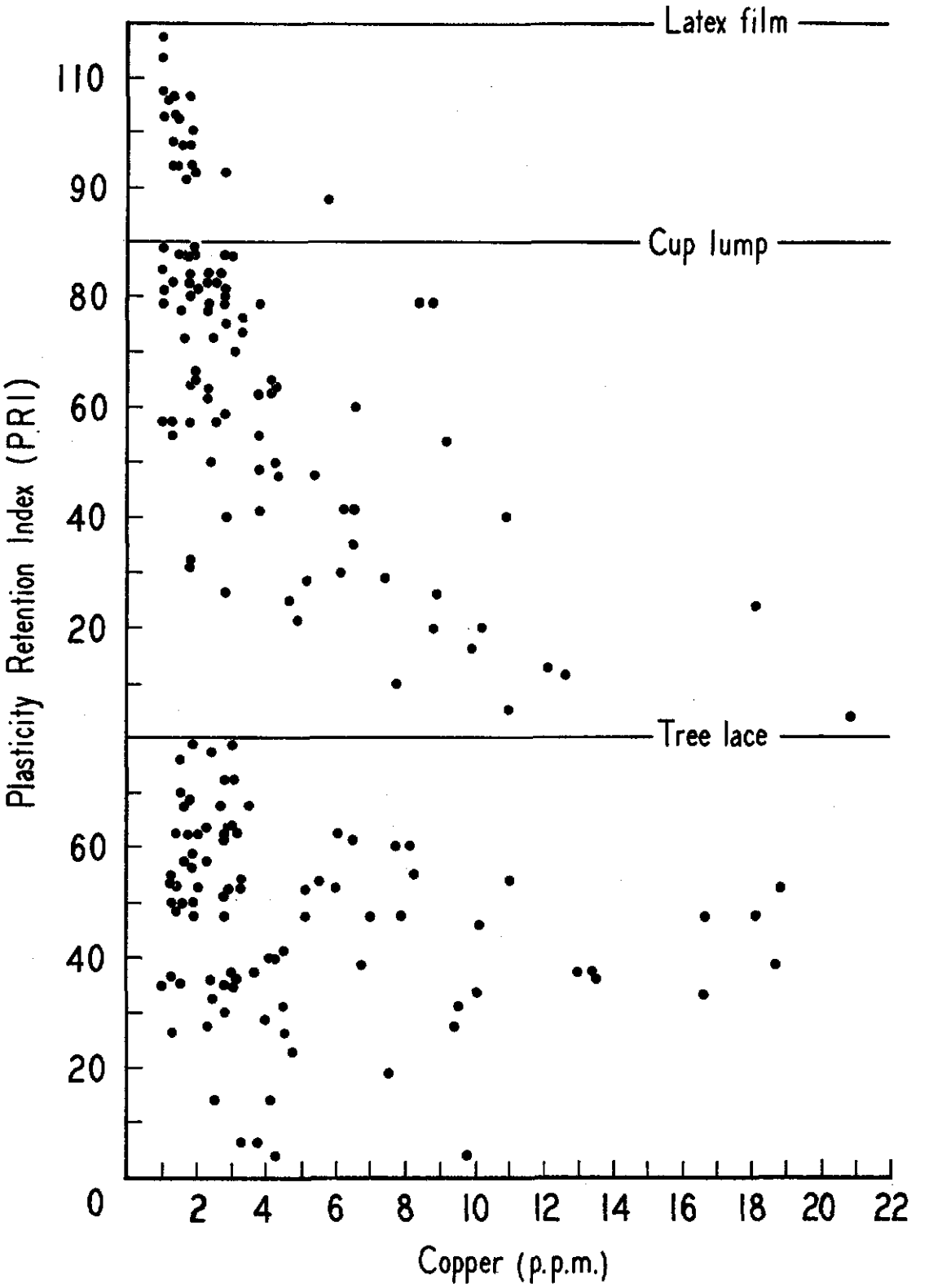

Figure 2. Relationship between PRI and copper content of latex film, cuplump and tree lace. Data from three experiments.

period of two months is a realistic length of time to allow between copper spraying and bringing trees into tapping.

Spraying copper fungicides in normal amounts to foliage from the air or ground for the control of leaf diseases would appear to be unlikely to result in unacceptable contamination of latex. No information has been obtained on the long-term effects of frequent applications of copper fungicides, but an annual application, such as might be necessary to control *Phytophthora* leaf fall, would present no undue hazard. It should be noted too that copper present in fresh latex can be largely removed with the serum during coagulation, so that rubber manufactured from latex with a high initial copper content has a low copper value (HEINISCH *et al.*, 1961a). To reduce contamination in the scrap grades tapping cups should be inverted during spraying, and it would be prudent to check the copper content of such rubber at frequent intervals. If contamination is severe it can be reduced by the methods suggested by HEINISCH *et al.* (1961b).

Figure 2 indicates that PRI may be used as a guide to the degree of copper contamination, for it shows that although there is no direct relationship between the two, a lower PRI frequently reflects a higher copper content. Only a small range of PRI/copper correlations was obtainable from the latex samples, but this tendency can nevertheless be seen. It is more marked with the scrap grades, where a copper content greater than 8 p.p.m. is associated with a PRI of less than 80 for cuplump and less than 60 for tree lace. However, *Figure 2* also shows that abnormally low PRI is not necessarily correlated with abnormally high copper, for a cuplump PRI of 30 or less may have a copper content between 2.8 and 20.9 p.p.m.; similarly a tree lace PRI of 40 or less may have a copper level between 1.0 and 18.8. There appears to be a better correlation between PRI and copper for cuplump than tree lace.

ACKNOWLEDGEMENT

Thanks are due to Dr R.C.H. Hsia and colleagues in the Analytical Chemistry Division for the copper analyses.

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Kuala Lumpur *September 1967*

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