J. Rubb. Res. Inst. Malaysia, 29(3), 146 – 154

Reaction of Dithiocarbamyl Compounds with Copper in Latex

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Copper occurs naturally in Hevea *latex mainly in soluble form. Its presence in latex and rubber is known to affect the raw and vulcanisate properties of rubber, particularly oxidation. The use of thiocarbamyl compounds in latex and rubber has been known for many years. They have been used as latex preservatives, antioxidants, accelerators and vulcanising ingredients. Water-insoluble dithiocarbamyl compounds such as tetraalkyl thiuram disulphide and zinc dialkyl dithiocarbamate are known to react with copper compounds. This paper describes a study of the reaction of copper with dithiocarbamyl compounds in latex. This reaction occurs at ambient temperature in the serum phase and yields sparingly-soluble compounds which are extracted by organic solvents and identified using ultraviolet-visible light spectroscopy and thin layer chromatographic analyses. This reaction also affects the distribution of copper between the rubber phase and serum phase. The significance of this finding in latex processing and properties is discussed.*

The use of dithiocarbamyl compounds in latex and rubber has been known for many years. They have been used as latex preservatives[1–4], antioxidants[5, 6], accelerators[7] and vulcanising ingredients[5]

Copper occurs naturally in *Hevea* latex. The majority of it is soluble in the serum fraction. Part of the copper found in latex may be attributed to the absorption of metal-containing enzymes from the bark of the rubber tree[8].

Sodium dialkyl dithiocarbamates react with copper salts in aqueous medium to give the corresponding insoluble copper dialkyl dithiocarbamates. Other sparingly soluble dithiocarbamates such as zinc dimethyl dithiocarbamate (ZDMC) or thiuram disulphides such as tetramethyl thiuram disulphide (TMTD) react with copper compounds in chloroform or other organic solvents.

In the normal coagulation of natural rubber with formic acid, copper is soluble in the acidified serum and will be washed off leaving only a very low concentration of copper in the rubber. In such a rubber, the testing of copper need not be carried out and may be replaced by other more convenient oxidisibility tests such as the Plasticity Retention Index (PRI)[9]. Copper-reacting compounds such as dithiocarbamyl compounds when added to latex as preservatives may give rise to higher copper content and low resistance to oxidation in raw rubber.

This paper describes a study of the reaction of copper with dithiocarbamyl compounds in latex serum and latex. The reaction results in the precipitation of insoluble copper dithiocarbamates in rubber. Analyses were performed using thin layer chromotography (TLC) and UV-visible light spectroscopy. The effects of the formation of these compounds on preservation of latex and the resistance of raw and vulcanised rubbers to oxidation are also discussed.

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MATERIALS AND METHODS

Field latex was obtained from the Rubber Research Institute of Malaysia Experiment Station in Sungei Buloh. Only stable latex from normal tapping was collected and immediately treated with ammonia at 0.3% weight/weight on latex. Sodium diethyl dithiocarbamate (SDC) was obtained from Rhône Poulenc; and TMTD, tetraethyl thiuram disulphide (TETD), zinc diethyl dithiocarbamate (ZDC) and ZDMC from ICI (Vulcafor range of chemicals). Copper dimethyl (CuDMC) and diethyl (CuDC) dithiocarbamates (cumate and ethyl cumate respectively) were obtained from Bayer. The water insoluble accelerators were purified by crystallising several times from hot chloroform by addition of 95% ethanol; TMTD and TETD by a published method[10]; and SDC by crystallisation from a hot saturated aqueous solution.

Ultracentrifugation was performed in a laboratory Spinco L centrifuge for 45 min at 19 000 r.p.m. (max. 47 000 g)[11]. Reaction of latex with dithiocarbamyl compounds was effected by mixing a ballmilled dispersion of the insoluble substances or an aqueous solution of water-soluble substances with latex and the mixture was well stirred and allowed to react for 1 h at room temperature.

A UV-visible light spectrum was obtained in a Spectronic 505 (Bausch and Lomb). CuDC and CuDMC in amyl alcohol absorbed at 435 nanometres[12–18].

For chromatographic analysis[19–22], the acetone solution of extracted substances, concentrated if necessary, was spotted on a TLC plate (Merck, Silicagel 60 F 254) and developed with toluene: ethyl acetate (9 : 1). CuDC and CuDMC appeared as green and brown spots respectively.

Quantitative determination of copper was carried out by atomic absorption[23]. In this method, 10 g of rubber were ashed, digested in nitric acid, made up to volume and the absorbance measured. Alternatively, dried serum was digested in 15 ml nitric acid: perchloric acid mixture (2 : 1), then dissolved in nitric acid and made up to volume.

RESULTS AND DISCUSSION

Reaction in Serum

Selected dithiocarbamyl compounds were added to various portions of serum (I) obtained by ultracentrifugation. Within a few minutes the serum samples changed from light to dark brown and became cloudy. Dithiocarbamyl compounds reacted rapidly at ambient temperature in latex serum. Van Gils[24] has proposed a mechanism of solubilisation for sulphur in latex serum. Whether sparingly soluble dithiocarbamyl compounds such as TMTD, TETD, ZDC or ZDMC are 'solubilised' in latex serum prior to their reactions with copper by the same mechanism is not known in the present experiments. In one such experiment, the reacted serum was recentrifuged to give a clear serum (II) and a brown residue. The results of analysis of the sera (II) are given in *Table 1*.

The resultant copper concentration in serum (II) is reduced by treating with TMTD. More than 70% of copper was removed on treating serum with $4 \times 10^{-3} M$ concentration of TMTD. It was not clear why a high concentration of TMTD was necessary to remove copper from serum.

The experiments were repeated with TMTD and TETD as the reactants and the results are shown in *Table 2*.

TABLE 1. REACTION OF DITHIOCARBAMYL COMPOUNDS IN SERUM

Serum sample number	Concentration of TMTD on serum (I) ($\times 10^{-3}$ *M*)	Concentration of Cu on serum (II) $\times 10^{-6}$ *M*	%	Molar ratio of TMTD/ Cu removed
1	Nil (control)	48	100	–
2	1	23	48	40
3	4	14	23	118

TABLE 2. REACTION OF DITHIOCARBAMYL COMPOUNDS IN SERUM

Serum sample number	Concentration of TMTD on serum (I) ($\times 10^{-3}$ *M*)	Concentration of Cu on serum (II) $\times 10^{-6}$ *M*	%	Molar ratio of TMTD/ Cu removed
1	Nil (control)	26	100	–
2	4 (TMTD)	11	42	267
3	4 (TETD)	9	36	235

The results in *Tables 1* and *2* showed some discrepancy but no reproducibility tests or rigorous quantitative determinations of the efficiency of copper removed by dithiocarbamyl compounds were attempted.

Analyses of Reacted Compounds

Various selected dithiocarbamyl compounds were added to various portions of serum (I) obtained by ultracentrifugation and the reacted mixture was recentrifuged, as described in the previous section. The residue in the ultracentrifugation tubes, after the serum (II) had been removed, was dried and extracted with acetone. The acetone extracts were spotted on TLC plates together with authentic samples of CuDMC and CuDC and the chromatogram was developed. The reacted substances were identified as CuDMC or CuDC *(Table 3)*.

The spots were scraped off the TLC plates and dissolved in amyl alcohol. The absorbance was shown to be strongest at 435 nanometres.

Effect of pH

In converting field latex or skim latex to dry rubber, such latices are acidified with formic acid or sulphuric acid to pH 5–5.2 (lower for skim latex). The effect of pH on the formation of CuDMC or CuDC will be of utmost importance. In an experiment, serum obtained by ultracentrifugation was divided into two portions and both of them were treated with 1×10^{-3} *M* concentration of TMTD. After 1 h, one of the two treated samples was acidified with 2% formic acid to pH 5. Both samples were recentrifuged to give a brown residue. The spectrum obtained from an amyl alcohol extract of the residue showed a peak at 435 nm and

TABLE 3. CHROMATOGRAM OF REACTED COMPOUNDS

Residue from ultracentrifuged mixtures of	Approximate R_F	Colour of spots
SDC + serum (I)	0.55	Green
ZDC + serum (I)	0.55	Green
TETD + serum (I)	0.55	Green
TMTD + serum (I)	0.46	Brown
ZDMC + serum (I)	0.46	Brown
CuDC standard	0.55	Green
CuDMC standard	0.46	Brown

both extracts showed approximately equal absorbance.

Re-distribution of Copper

The reaction between dithiocarbamyl compounds and copper ions in latex and latex serum may be illustrated as follows:

For thiuram disulphides

$$R_2\,N\,\overset{\overset{S}{\|}}{C}\,S\,S\,\overset{\overset{S}{\|}}{C}\,N\,R_2 + Cu^{2+} \longrightarrow (R_2\,N\,\overset{\overset{S}{\|}}{C}\,S)_2\,Cu$$

For zinc dialkyl dithiocarbamates

$$(R_2\,N\,\overset{\overset{S}{|}}{C}\,S)_2\,Zn + Cu^{2+} \longrightarrow (R_2\,N\,\overset{\overset{S}{\|}}{C}\,S)_2\,Cu + Zn^{2+}$$

In a recent review, Satchell[25] discussed the cleavage reaction of disulphides promoted by metal ions such as silver and copper and noted that disulphides with chelating possibilities tend to react rapidly and sometimes render one metal ion very much more effective than others. Philpott[5] discussed the cleavage reaction of TMTD but noted that such cleavage proceeded only at a reasonable rate at elevated temperature (100°C) in the presence of thiourea which acted as a catalyst. He inferred that copper dialkyl dithiocarbamates were formed and that these were harmless to rubber. He did not consider the reaction of TMTD with copper, shown in the present work to proceed at room temperature in the absence of a catalyst.

Mellor and Maley[26] drew up an order of stability of metal complexes and placed the metals in the following order Cu > Zn > Cd > Fe > Mn > Mg. In other words, if one metal complex is more stable than another of the same type, under suitable conditions, a metal will displace another from a less stable complex. The findings in the present study are consistent with their order of stability.

The precipitation of copper in the form of CuDMC or CuDC has very important implications in the processing of rubber and latex concentrate, especially since the reaction is not affected by pH of the latex. CuDMC and CuDC are insoluble and are occluded in the rubber coagulum. The effect will give rise to a high copper content in the resultant rubber. To demonstrate that copper is re-distributed on reacting the latex with dithiocarbamyl compounds, the following experiment was conducted. Ammoniated field latex was treated with 1×10^{-3} *M* concentration of TMTD and the treated sample was then ultracentrifuged into three fractions. A control was similarly prepared except for the treatment with TMTD. The three fractions were analysed for copper. Results of analysis[27] on the three fractions separated by ultracentrifugation are shown in *Table 4.*

Manganese and iron are not capable of displacing the zinc ion in the dithiocarbamyl compounds and as such their dithiocarbamates were not detected in present tests.

TABLE 4. REDISTRIBUTION OF COPPER IN VARIOUS ULTRACENTRIFUGED FRACTIONS

Latex fraction	Copper[a] (μ mole)	
	NH_3 latex	NH_3 – TMTD latex
Rubber cream	2.4	7.6
C serum	18.0	8.8
B fraction	0.5	3.8
Total	20.9	20.3

[a]Based on 1 litre of latex

TABLE 5. EFFECT OF CRUMB TREATMENT ON PLASTICITY RETENTION INDEX

Treatment on skim latex	Soaking treatment of crumb	P_o	PRI (%)	Cu (μ mole/kg rubber)
Nil (control)	Nil	69	49	31
1×10^{-3} *M* TMTD	Nil (control)	65	11	375
TMTD	Glycine	73	41	375
TMTD	Thiourea	69	78	375
TMTD	Polyamine D	60	40	289
TMTD	EDTA	69	10	393

Effect of Competing Ligands

In block rubber processing, it is imperative to treat rubber of low PRI with chelating agents to improve its resistance to oxidation[28]. Presumably this treatment allows pro-oxidant such as copper ion to react with the chelating agents, thereby rendering copper harmless. Commonly used agents are thiourea, phosphoric acid, oxalic acid and ethylene diamine tetra-acetic acid (EDTA).

Skim latex was treated with 1×10^{-3} *M* concentration of TMTD prior to coagulation with sulphuric acid. The rubber after creping and crumbling was divided into different portions and soaked separately in 2% solutions of various chemicals (in the ratio of 3 : 1 of treatment solution to wet crumb weight) for an hour. The crumbs were dried and tested for PRI and copper content *(Table 5)*.

Soaking of skim rubber crumb in solutions of chelating agents especially thiourea improves PRI of the rubber compared with control (no soaking). This phenomenon is somewhat surprising since copper reacts with dithiocarbamate in preference to other ligands.

To demonstrate the effect of competing ligands on the formation of CuDMC or CuDC, glycine, thiourea, Polyamine D and EDTA were added at 4×10^{-3} *M* concentration to separate portions of ultracentrifuged serum (I). Two hours later, TMTD or ZDC was added and the serum was allowed to react further for an hour. The reacted serum samples were recentrifuged to give a clear serum (II) and a brown residue. The latter, on extraction with amyl alcohol and tested by UV-visible light spectroscopy, showed the presence of CuDMC or CuDC. Since copper reacts with dithiocarbamates preferentially over other ligands and the CuDMC or CuDC formed are water insoluble, there is no simple means to prevent the precipitation of copper in rubber.

Effect on Rubber Processing

Ammoniated skim latex was treated with SDC, ZDC and TMTD at 1×10^{-3} *M* concentration on latex respectively. The samples were coagulated adding formic acid to pH 5. The rubber were subsequently creped and dried. Results of tests on the rubber are shown in *Table 6*.

TABLE 6. PRECIPITATION OF COPPER IN RUBBER

Chemical (1×10^{-3} M)	P_o	PRI (%)	Concentration of Cu on rubber (μ mole/kg)	%
Control (no treatment)	59	65	58	100
SDC	59	17	197	339
ZDC	58	21	184	317
TMTD	56	50	217	374

Similar test results were obtained on field latex treated with dithiocarbamyl compounds. Percentage PRI obtained showed that the CuDMC or CuDC formed affected the resistance of *raw* rubber to oxidation.

To provide more evidence of the effect of copper dialkyl dithiocarbamates in rubber, normal skim rubber was treated with CuDMC at two concentrations by milling in the solid chemical to the dry rubber. The well-mixed rubber samples were tested for PRI and results are shown in *Table 7.*

At the lower concentration of CuDMC, resistance to oxidation was lower whereas at a higher concentration (1650×10^{-6} mole per kilogramme), resistance to oxidation was unaffected compared with control. The finding may be compared with those of previous workers. Blackley and Mahmood[6] have shown that a concentration of 500×10^{-6} mole per kilogramme of CuDC on rubber was not harmful to the ageing of vulcanisates. Philpott[5] has also found that CuDMC at 5500×10^{-6} mole per kilogramme concentration was an excellent antioxidant.

TABLE 7. EFFECT OF COPPER DIMETHYL ON PLASTICITY RETENTION INDEX

CuDMC (μ mole/kg)	P_o	PRI (%)
Control	44	74
550	43	33
1 650	44	72

Effect on Preservation

A widely held view in the preservation of latex is the role of sulphydryl proteins and their degradation by bacteria or bacterial enzymes[4]. The degradation products combine with glucose to form a glucose-amino acid complex which is then metabolised to volatile fatty acids[29]. Substantiating this view is the effectiveness of some chemicals which react with sulphydryl group and inactivate the sulphydryl protein in the preservation of latex[4].

Findings from the present study suggest the possible important role of the inactivation of copper in preservation. Copper and other metals are important constituents of enzyme in biological systems and are essential for metabolism of various substrates. However, these enzymes may be inactivated by added chelating agents which compete with the enzymes for the metal[30]. Albert and co-workers[31, 32] cited the use of SDC, oxine, mercaptobenzthiazole and potassium ethyl xanthate (PEX) as bactericidal chelating agents in broth medium at pH 7.3. These compounds chelate copper and other metallic ions and all, except PEX, are known latex preservatives[3, 33, 34]. An isopropyl substituted xanthate[3] has been successfully tried as a latex preservative.

The minimum effective levels of preservatives reported are shown in *Table 8.*

The average concentration of copper in latex is about 20×10^{-6} mole per litre. This may be compared with the minimum concentration of preservatives found for the various dithiocarbamyl compounds as shown in *Table 8*. Lack of substantiating experimental evidence precludes any conclusion on the causal relationship between copper inactivation and latex preservation.

TABLE 8. EFFECTIVE LEVEL OF DITHIOCARBAMYL PRESERVATIVES

Preservative	Effective level on latex (%)	Chemical conc. on latex (10^{-6} mole/ litre)	Ref.
SDC[a]	0.005	220	34
TMTD[a]	0.013	540	35
ZDC	0.015	410	33

[a]Requires zinc oxide

CONCLUSION

Dithiocarbamyl compounds react rapidly with copper in latex at ambient temperatures forming copper dithiocarbamates. The reaction results in the redistribution of copper in the various phases of the latex on ultracentrifugation and this precipitation of copper results in the high copper content of rubber derived from latex preserved with dithiocarbamyl compounds. The presence of copper dithiocarbamates at relatively high concentrations does not affect the resistance of rubber vulcanisates towards oxidation as shown by previous workers. As dithiocarbamate is a stronger ligand than many of the copper-chelating ligands, there is as yet no known means of reducing the high copper content of rubber derived from latex treated with dithiocarbamyl compounds.

ACKNOWLEDGEMENT

The author wishes to thank Dr A. Subramaniam for his interest in the work and for helpful suggestions in the preparation of the manuscript; Mr Cheong Sai Fah and Dr Chen Seong Fong for useful discussions; Mr Chin Hong Cheaw and staff of the Analytical Chemistry Division for the determination of copper content and for taking the spectra; Mr E.S. Wee, Cik Norhanam bte Sulong and Mr S. Puvanendran for experimental assistance.

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Kuala Lumpur *May 1981*

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