

## ***Effect of Adventitious Iron on Epoxidation of Natural Rubber Latex***

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*The epoxidation of natural rubber using hydrogen peroxide and formic acid is perturbed by the presence of adventitious iron(II), due to the interference of chemistry associated with Fenton's Reagent and the facile generation of hydroxyl radicals. The extent of intervention is dependent on the concentration of iron(II) and can result in retardation of the rate of epoxidation due to the depletion of hydrogen peroxide, enhanced oxidative degradation and a reduction in the gel content of the rubber. Degradation of the surfactant leads to destabilisation of the latex and premature coagulation of the polymer for iron(II) concentrations above 10 p.p.m. Fenton's Reagent may be useful as a chemical method to depolymerise polyisoprenoid latices at iron(II) concentrations above 50 p.p.m. However, vigorous gas and heat evolution and premature coagulation of the polymer can result in an uncontrollable and potentially hazardous reaction.*

Epoxidised natural rubber (ENR) can be prepared by the epoxidation of natural rubber (NR) latices with performic acid generated *in situ* from hydrogen peroxide and formic acid<sup>1</sup>. ENR 50 (*i.e.* 50 mole% epoxidised NR) is routinely prepared in our laboratories from high-ammonia (HA) latex concentrate using a standard recipe, but significant variations in the rate of epoxidation and epoxy group content of the product were observed in several preparations. The source of variability was found to be associated with the substrate latex rather than acid-catalysed hydrolytic reactions accompanying epoxidation<sup>2</sup> and therefore chemical species<sup>1</sup> which varied significantly in concentration between individual batches of latex were scrutinised. NR latex concentrates of Malaysian origin are subject to strict quality control<sup>3</sup> and it is unlikely that any species which affects the physical properties of latex concentrates is not monitored before shipment. However, it is known that rupture of the lining in drums of latex during handling and transportation

can give rise to a considerable variation in the iron content of HA latex concentrate. Iron contents within the range of 2–250 p.p.m. have been measured with an average iron content<sup>4</sup> of 50 p.p.m. found for concentrate that has been stored in drums. The iron content of fresh latex concentrate has been found<sup>5</sup> to vary between 0.5 p.p.m. and 5 p.p.m.

This paper records the results of a series of latex epoxidations in which variability between reactions was monitored as a function of iron(II) content.

### EXPERIMENTAL

#### **Epoxidation of HA Latex**

Texofor A60 (108 g, 5% aq, 5.4 g, 3 p.h.r. ABM Chemicals), a non-ionic surfactant, was stirred into HA latex (300 g, 60% d.r.c., 180 g, 2.65 moles isoprene units) over 30 min in an oil bath at 60°C. Formic acid (20 ml, 98%, 0.52 moles), diluted with distilled

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water (100 ml), was added dropwise followed by rapid addition of hydrogen peroxide (115 ml, 50% w/w, 2.03 moles). The epoxidation reaction was taken to commence after complete addition of the hydrogen peroxide. Specific concentrations of iron(II) were added to each reaction mixture using hydrated iron(II) ammonium sulphate (98%) dissolved in the aqueous formic acid. Each reaction was sampled hourly; latex samples were coagulated in methylated spirits containing a molar excess of aqueous sodium hydroxide (2M), leached in distilled water and dried *in vacuo* at 50°C. Samples of prematurely coagulated polymer were leached in distilled water containing a molar excess of sodium hydroxide before washing and drying. At iron(II) concentrations above 50 p.p.m., these reactions become highly exothermic; vigorous foam formation coupled with premature coagulation of the polymer can result in uncontrollable and hazardous reactions.

#### Control Reaction for Epoxidation of HA Latex

In this reaction, distilled water was substituted for the latex and hydrated iron(II) ammonium sulphate (0.2342 g, 98%,  $5.85 \times 10^{-4}$  moles) was dissolved in the reaction mixture to yield an iron(II) concentration of 49 p.p.m. After 5½ h (*i.e.* the time at which coagulation of the polymer occurred in the analogous latex epoxidation), the reaction was sampled and assayed for hydrogen peroxide content. The reaction bulk was treated with aqueous sodium hydroxide (4M) until a red-brown solid precipitated. After standing overnight, the precipitate was filtered and the filtrate extracted with diethyl ether (2 × 500 ml, dried with sodium wire). After drying over anhydrous magnesium sulphate, filtration and rotary evaporation yielded a small amount of a beige wax.

#### <sup>1</sup>H-NMR Spectroscopy

The epoxy group content of samples from latex epoxidation was determined using

<sup>1</sup>H-NMR spectroscopy. <sup>1</sup>H-NMR spectra were acquired at a Larmor frequency of 200 MHz using a Varian XL-200 NMR spectrometer. Quantitative data<sup>6</sup> was collected for sol fractions, prepared as 1% w/v solutions in deuteriated chloroform (CDCl<sub>3</sub>).

#### Estimation of Hydrogen Peroxide

Latex aliquots (5 ml) were diluted to 100 ml with distilled water and cooled to 4°C–5°C in an ice bath. Aliquots (10 ml) of the diluted mixture were titrated against acidified cerium (IV) sulphate (0.05M, BDH Convol) using ferroin as indicator.

#### Separation of Sol and Gel Fractions

ENR samples were separated into sol and gel fractions by swelling of the whole polymer at 0.5%–1.0% w/v in CDCl<sub>3</sub> for 24–48 h at 5°C, with subsequent filtration through lens tissue to recover the sol fraction<sup>7</sup>.

## RESULTS AND DISCUSSION

#### Physical Effects of Iron(II) Content on Epoxidation of NR Latex

It is known that the total iron content of latex concentrates can vary widely<sup>4</sup> due to contamination during shipment and hence the effect of iron was investigated using a step-wise enhancement of iron concentration in epoxidation using HA latex concentrate from a single drum.

Initial studies were based on latex with a total iron content of 4.8 p.p.m. as determined by atomic absorption spectrometry (AA). The standard AA procedure<sup>8</sup> for the assay of iron content in NR is based on conversion of all the iron present to iron(II) chloride and hence the absolute concentration of iron in its three common oxidation states (0, +2 and +3) was not measured. The concentration of total iron in an undoped epoxidation reaction was calculated to be 2.2 p.p.m. (based on total reaction volume) and therefore assumed to be negligible; the

effect of iron(II) content was examined over a concentration range of 0–100 p.p.m. (equivalent to 0–214 p.p.m. in an undoped latex) by doping with iron(II) ammonium sulphate. These studies were concentrated on the specific effect of iron(II) because the primary iron(III) species present in an adulterated drum of latex is rust, which is chemically passive; in addition, iron(II) is known to react with hydrogen peroxide to form a potent oxidising system. A standard ENR 50 preparation is generally well behaved with no heat evolution, minimal foaming and an apparent pH of 3.8. As the concentration of iron(II) was progressively increased to 100 p.p.m., several effects were observed; foam formation, the production of steam in exothermic reactions, an increase in reaction basicity and *in situ* coagulation of the polymer (*Table 1*). At iron(II) concentrations above 50 p.p.m., rapid coagulation of the polymer can lead to the formation of a thick polymer film covering a serum which is

expelling large volumes of steam and oxygen; the resultant build-up of pressure makes this reaction potentially hazardous.

Vigorous gas evolution and an increase in basicity are effects consistent with the reaction of iron(II) with hydrogen peroxide, a reagent combination known as Fenton's Reagent. Fenton's Reagent (and its transition metal analogues) considerably enhance the otherwise mild oxidising power of hydrogen peroxide *via* the facile generation of hydroxyl radicals<sup>9,10</sup> in a free radical chain mechanism<sup>11,12,13</sup> (*Figure 1*). A catalytic cycle can be established (*Steps 1, 4 and 5 in Figure 1*) which results in the regeneration of iron(II) and catalytic decomposition of hydrogen peroxide to generate oxygen, hydroxide ions and hydroxyl radicals. Foaming in the initial stages of reaction is consistent with the evolution of oxygen and the apparent increase in reaction basicity is consistent

TABLE 1. PHYSICAL BEHAVIOUR OF LATEX EPOXIDATIONS IN THE PRESENCE OF IRON(II)

Iron(II) concentration (p.p.m.)	Physical behaviour
0 <sup>a</sup>	Minimal foam formation A stable latex after 24 h at 60°C Apparent final pH = 3.8
10	Minimal foam formation Premature coagulation after 18–22 h Apparent final pH = 4.0
50	Considerable foam formation Some steam generation Premature coagulation after 5½ h Apparent final pH = 4.4
50 <sup>b</sup>	Vigorous gas evolution Maximum reaction temperature = 75°C Serum pH = 1.9
100	Uncontrollable foaming at the start of reaction Copious steam generation Maximum serum temperature = 98°C Premature coagulation after 85 min Final serum pH = 6.8

<sup>a</sup>Total iron content in this reaction = 2.2 p.p.m.

<sup>b</sup>Control reaction in which distilled water was substituted for latex.

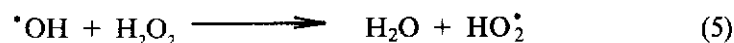
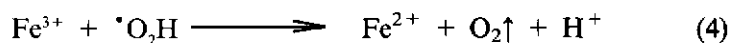
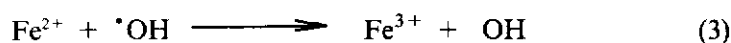
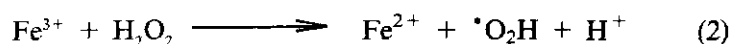


Figure 1 Generation of hydroxyl radicals by Fenton's Reagent

with the generation of hydroxide ions. Since Fenton's Reagent leads to the consumption of hydrogen peroxide, iron(II) in latex epoxidations would be anticipated to lead to an enhanced depletion of hydrogen peroxide due to competition between iron(II) and epoxidation chemistry. The measurement of residual hydrogen peroxide content during latex epoxidation (Table 2) can be used to define a *conversion efficiency* for hydrogen peroxide usage by relating the consumption of hydrogen peroxide to the epoxy group content of the polymer (as a percentage), it is evident that conversion efficiencies are lowered as the iron(II) content is increased (Table 2). An increase in the concentration of iron(II) from 0 to 10 p p m leads to a loss

in conversion efficiency of 23 mole% over 24 h reaction and demonstrates the potential significance of Fenton's Reagent during latex epoxidation. Premature coagulation of the polymer at higher concentrations of iron(II) (Table 1) complicates the interpretation of results, but a control reaction at an iron(II) concentration of 49 p p m. (in which distilled water was substituted for HA latex) resulted in the consumption of 24 mole% hydrogen peroxide in 5<sup>1</sup>/<sub>2</sub> h.

#### Fenton's Reagent and Rate of Epoxidation of NR Latex

The epoxidation of NR latices using performic acid generated *in situ* from

TABLE 2 CONSUMPTION OF HYDROGEN PEROXIDE AS A FUNCTION OF IRON(II) CONTENT

Iron(II) concentration (p p m)	Residual hydrogen peroxide (mole%)	Conversion efficiency H <sub>2</sub> O <sub>2</sub> -> ENR (%)
0	21 <sup>a</sup>	92
10	9	69
50	48 <sup>b</sup>	69 <sup>c</sup>
50 <sup>d</sup>	76 <sup>e</sup>	—
100 <sup>f</sup>	—	—

<sup>a</sup>24 h reaction

<sup>b</sup>24 h reaction premature coagulation occurred after 5<sup>1</sup>/<sub>2</sub> h

<sup>c</sup>Assumed

<sup>d</sup>Control reaction

<sup>e</sup>After 5<sup>1</sup>/<sub>2</sub> h

<sup>f</sup>Uncontrollable foaming precluded sampling

hydrogen peroxide and formic acid is a reaction in which the formation of performic acid in the aqueous phase is the rate-controlling step<sup>14,15</sup>. The reaction can be considered as pseudo-first order for hydrogen peroxide because formic acid is regenerated when the peracid reacts with the alkene bonds in NR (Figure 2). Iron(II) leads to the catalytic decomposition of hydrogen peroxide and generates hydroxide ions (Figure 1) and therefore results in the consumption of both hydrogen peroxide and formic acid. Campbell has shown that formate ions do not promote peracid formation with hydrogen peroxide<sup>16</sup> and Fenton's Reagent would be predicted to retard the rate of NR latex epoxidation. In addition, the relative reaction rates for the catalytic decomposition of hydrogen peroxide and formation of performic acid should determine the maximum epoxy group content in the polymer (although in practice, the use of a large excess of hydrogen peroxide in the epoxidation recipe makes it unlikely that adventitious iron(II) could prevent the ultimate preparation of ENR 50). The epoxy group content of samples was determined using <sup>1</sup>H-NMR spectroscopy<sup>6</sup>; care was taken to ensure that samples were coagulated under basic conditions to prevent the acid-catalysed

ring-opening of epoxy groups. The results (Figure 3) clearly indicated a progressive retardation in the rate of polymer epoxidation as the concentration of iron(II) was increased, as expected for interference from iron(II) and chemistry associated with Fenton's Reagent.

### Fenton's Reagent and Oxidation of NR

The primary application of Fenton's Reagent (and analogues) in synthetic chemistry lies in the facile generation of hydroxyl radicals since this species is recognised as a powerful oxidising reagent which is capable of abstracting hydrogen atoms from most organic substrates (Figure 4). Fenton's Reagent has therefore been used extensively to oxygenate many organic compounds<sup>12,13</sup>. Iron(II) is also known to catalyse the decomposition of alkyl hydroperoxides via a catalytic cycle similar to that generated by Fenton's Reagent<sup>9,17</sup>. The autoxidation of NR with oxygen is propagated by the abstraction of allylic hydrogen atoms and initiated by the decomposition of rubber-bound hydroperoxide groups<sup>18,19</sup>. Although the exact mechanism for oxidative scission in NR is unknown<sup>20</sup>, it is evident that Fenton's Reagent can enhance the rate of NR oxidation (Figure 5) due to three factors:

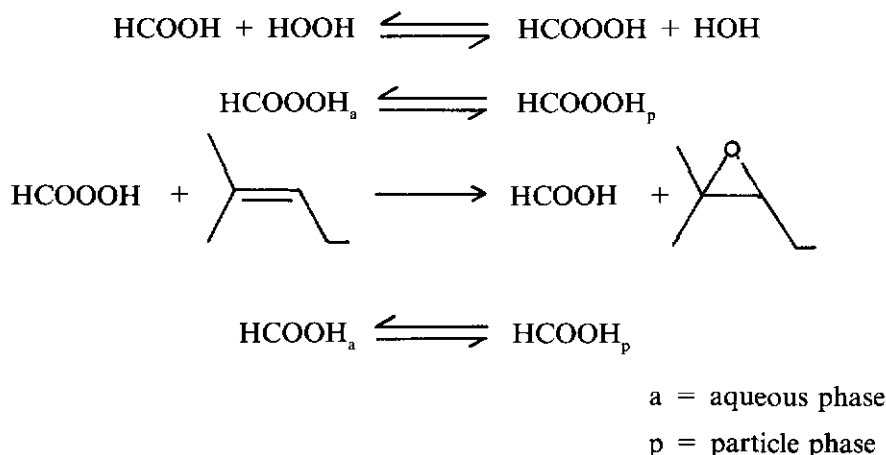


Figure 2. Mechanism for the epoxidation of NR latex from hydrogen peroxide and formic acid.

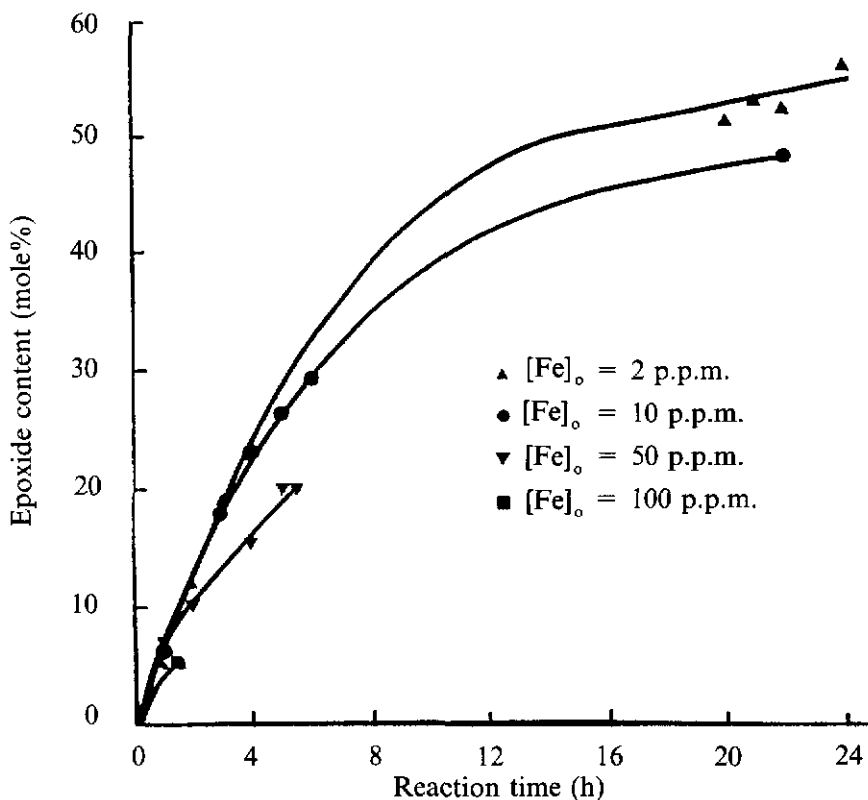


Figure 3. Rate of epoxidation of NR latex as a function of iron(II) concentration.

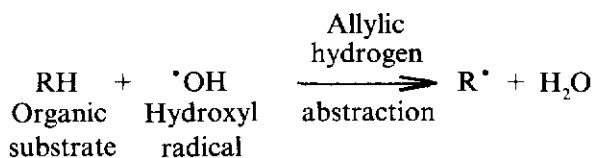


Figure 4. Hydrogen atom abstraction by hydroxyl radicals.

- The increased availability of oxygen arising from the catalytic decomposition of hydrogen peroxide
- An increase in propagation rate due to the facile abstraction of allylic hydrogen atoms from NR by hydroxyl radicals
- An increase in the overall rate of autoxidation due to iron(II)-catalysed decomposition of rubber-bound hydroperoxide groups.

Trace metal catalysis in the autoxidation of alkenes<sup>21,22</sup> and polyisoprenoids has been studied; Mayo and co-workers<sup>23</sup> reported the

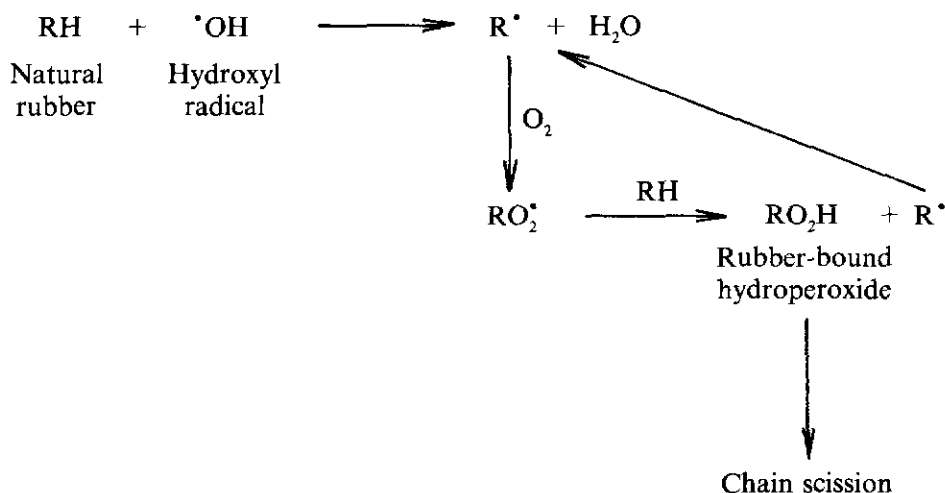


Figure 5. Fenton's Reagent and enhanced oxidative scission in NR.

catalytic effect of transition metal ions on the autoxidation of polyisoprenoids in solution and Bevilacqua<sup>24,25</sup> attributed the rate of aerobic oxidation in NR latices to adventitious metal ions acting as catalysts. It is also likely that a patented technique for the depolymerisation of NR latices which uses hydrogen peroxide<sup>26</sup> operates through the adventitious presence of iron(II) and other metal ions.

The tackiness of ENR which has prematurely coagulated from latex epoxidation in the presence of 10–100 p.p.m. iron(II) ions is evidence for enhanced oxidative scission and this is confirmed by molecular weight and gel content data (Table 3). In general, concentrations of iron(II) above 10 p.p.m. promote NR autoxidation and eliminate gel content. The extent of oxidative scission found for ENR prepared in the presence of iron(II) concentrations above 50 p.p.m. results in the synthesis of highly depolymerised products (known as 'liquid rubbers'<sup>32</sup>) and Fenton's Reagent may therefore be promoted as a chemical method to depolymerise polyisoprenoid latices<sup>26</sup>.

#### Fenton's Reagent and Destabilisation of Latices

Experimental results indicated a correlation between the concentration of iron(II)

and the destabilisation of latices (Table 1) and the most plausible explanation for this behaviour is based on chemical degradation of the surfactant. Texofor A60 is a mixture of two polyethers (Figure 6) and derives its surface activity from the combination of a lipophilic aliphatic- and a hydrophilic polyether-component in each molecule. Alkanes are resistant to Fenton's Reagent<sup>12,27</sup>, whereas aliphatic ethers readily undergo fragmentation to yield aldehydes and alcohols<sup>12,28,29</sup> (Figure 7). Experimental evidence for the degradation of Texofor A60 was pursued through a control reaction in which water was substituted for NR latex and the mixture doped with iron(II) at a concentration of 49 p.p.m. After 5½ h (the time at which coagulation occurred in the analogous latex epoxidation), the reaction was worked up by the precipitation of hydrated iron(III) oxide<sup>30</sup> and the extraction of organic species with ether. The waxy material recovered by extraction did not contain Texofor A60 since it was shown that diethyl ether does not extract this surfactant from water. <sup>1</sup>H-NMR spectroscopic analysis of the wax showed a multiplicity of -CH<sub>2</sub>-O-(H) resonances between 3.65 p.p.m. and 3.69 p.p.m. (compared with a predominant -CH<sub>2</sub>-O-resonance at 3.65 p.p.m. in Texofor A60) and several signals between 8 p.p.m.

TABLE 3 EFFECT OF FENTON'S REAGENT ON THE OXIDATION OF NATURAL RUBBER

Reaction time (h)	$10^5 M_n^a$	$10^6 M_z^b$	Gel content (wt%, THF <sup>c</sup> )
1 <sup>d</sup>	1.70	1.85	20
2	1.75	1.62	18
5	1.85	1.78	26
24	1.80	1.54	61
1 <sup>e</sup>	2.50	2.02	31
3	2.80	1.97	33
5	2.40	2.31	30
22 <sup>f</sup>	1.40	2.05	15
1 <sup>g</sup>	1.85	1.65	11
2	1.85	1.64	9
5	0.70	1.03	0
5 <sup>1/2</sup> <sup>d</sup>	0.45	1.44	0
1 <sup>1/2</sup> <sup>f</sup>	0.45	0.69	4

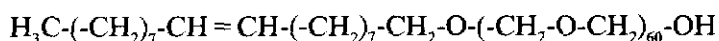
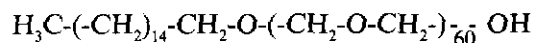
<sup>a</sup>Number-average molecular weight by GPC<sup>b</sup>Z-average molecular weight by GPC<sup>c</sup>Tetrahydrofuran<sup>d</sup>Iron (II) content = 2 p.p.m.<sup>e</sup>Iron (II) content = 10 p.p.m.<sup>f</sup>Premature coagulation of the polymer<sup>g</sup>Iron (II) content = 50 p.p.m.<sup>h</sup>Iron (II) content = 100 p.p.m

Figure 6. Chemical composition of Texofor A60.

and 10 p.p.m. which are not observed in Texofor A60 and are characteristic for aldehydes. The spectral data therefore contained evidence for the presence of alcohols and aldehydes in the wax and is consistent with fragmentation of the surfactant induced by hydroxyl radicals.

#### Estimation of Hydrogen Peroxide in Latex Epoxidation

The use of acidified cerium(IV) sulphate solution with ferroin as indicator to assay hydrogen peroxide is a standard analytical procedure<sup>31</sup> and has been used to monitor



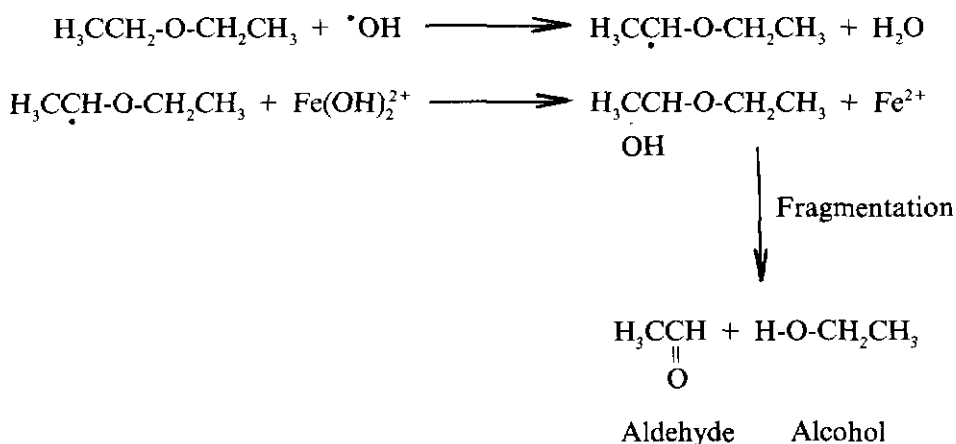


Figure 7. Fragmentation of ethers by hydroxyl radicals.

the consumption of hydrogen peroxide during latex epoxidation. At room temperature, the procedure has a transient colour change at the end-point and reversion is believed to result from the sluggish titration of performic acid. A solution of 0.1% hydrogen peroxide in 30% peracetic acid can be titrated at 0°C–10°C without interference from the peracid using cerium(IV) sulphate solution<sup>32,33</sup>. Hydroperoxides are sufficiently reactive to be titratable at 0°C – 10°C whereas diacyl and dialkyl peroxides are passive, and it is implicit in these results that peracids are titratable above a temperature of 10°C. Volumetric analysis of samples from a latex epoxidation demonstrated that analyses at 4°C–5°C and 20°C gave the same end-point if the first colour change at 20°C was taken. Reversion occurred within 20 s at 20°C while the end-point at 4°C–5°C was found to be stable.

#### Iron(II) Content in Drums of Latex Concentrate

It is evident that iron(II) in NR latices will interfere with any chemistry using hydrogen peroxide as a reagent and therefore the concentration of iron(II) in the adventitious iron content of latex is important if the effects of chemistry associated with Fenton's Reagent are to be assessed.

The standard method for the assay of iron in NR is non-specific<sup>8</sup> and therefore we can only speculate on the relative concentrations of iron(II) and iron(III) in a drum of latex concentrate. The main source of iron in latex concentrate is contamination from the inner surfaces of steel drums and probably consists of iron(III) oxides (*i.e.* rust). Aqueous solutions of iron(II) ions are susceptible to superficial oxidation by molecular oxygen, a redox reaction that will occur under acidic conditions, but is particularly favoured in basic media<sup>30</sup> (Figure 8). Neutral and acidic solutions of iron(II) ions oxidise less rapidly with increasing acidity due to the formation of hydroxo complexes. The basicity of ammoniated latex should result in the oxidation of any iron(II) present to iron(III); however, the addition of hydrogen peroxide to an acidified latex may regenerate iron(II) ions as illustrated (Figure 1, Step 2), causing the intervention of chemistry associated with Fenton's Reagent when the total iron content is high.

#### CONCLUSIONS

The epoxidation of NR latices using hydrogen peroxide and formic acid is perturbed by the presence of iron(II) due to interference from chemistry associated with Fenton's Reagent. The activity of Fenton's

Acidic conditions



Basic conditions

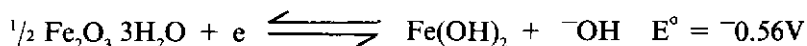


Figure 8. Redox reactions for iron (II)/(III) ions in acidic and basic conditions

Reagent is dependent on the concentration of iron(II) and can result in a marked retardation in the rate of epoxidation and enhanced oxidation of the polymer. Fenton's Reagent may be useful as a chemical method to depolymerise polyisoprenoid latices. Fenton's Reagent leads to the generation of oxygen from the catalytic decomposition of hydrogen peroxide and can also result in premature coagulation of the polymer by chemical degradation of the surfactant, the combination of these two factors can produce reactions which are potentially hazardous. The interference of performic acid during the volumetric assay of hydrogen peroxide using cerium(IV) sulphate solution is removed if titrations are conducted between 0°C and 10°C.

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REFERENCES

1. MALAYSIAN RUBBER PRODUCERS' RESEARCH ASSOCIATION (1982) Epoxidized *Cis*-1,4-Polyisoprene Rubber *U.K. Pat Appl No GB 2113692*
2. GELLING, I. R. AND PORTER, M. (1988) *Natural Rubber Science and Technology* (Roberts A. D. ed.), Chap. 10. Oxford: Oxford University Press.
3. INTERNATIONAL STANDARDS ORGANISATION (1979) Rubber Latex - Centrifuged or Creamed, Ammonia-Preserved Types - Specifications. ISO 2004.
4. PENDLE, T. D. Unpublished Data. Malaysian Rubber Producers' Research Association, United Kingdom.
5. GELLING, I. R. Unpublished Data. Malaysian Rubber Producers' Research Association, United Kingdom.
6. FARLEY, P. S. (1991) Unpublished Data. Malaysian Rubber Producers' Research Association, United Kingdom.
7. FARLEY, P. S. (1991) Geometrical Isomerisation of Polyisoprenes. Part 1. The Occurrence and Estimation of *Trans*-Alkene Functionality in Natural Rubber. *J. nat. Rubb. Res.* **6**(4), 215.
8. INTERNATIONAL STANDARDS ORGANISATION (1990) Rubber - Determination of Metal Content by Atomic Absorption Spectrometry. ISO 6101-5.
9. KOCHI, J. K. (1973) *Free Radicals* (Kochi J. K. ed.), Vol. 1, Chap. 11. New York: Wiley-Interscience.
10. KOCHI, J. K. (1973) *Free Radicals* (Kochi J. K. ed.), Vol. 2, Chap. 23. New York: Wiley-Interscience.

- 11 NORMAN, R O C AND WEST, P R (1969) Electron Spin Resonance Studies XIX Oxidation of Organic Radicals and the Occurrence of Chain Processes during the Reactions of Some Organic Compounds with the Hydroxyl Radical Derived from Hydrogen Peroxide and Metal Ions *J Chem Soc B*, 389
- 12 SOSNOVSKY, G AND RAWLINSON, D J (1971) *Organic Peroxides* (Swern D ed), Vol 2, Chap 2 New York Interscience
- 13 RAZUVAEV, G A, SHUSHUNOV, V A, DODONOV, V A AND BRILKINA, T G (1972) *Organic Peroxides* (Swern, D ed) Vol 3, Chap 1 New York Interscience
- 14 SHAPILOV, O D AND KOSTYUKOVSKII, L (1975) Reaction Kinetics of Hydrogen Peroxide with Formic Acid in Aqueous Solutions *Kinet Catal (Engl Transl)*, 15, 947
- 15 CAMPBELL, D S (1989) The Relevance of Phase Heterogeneity in Epoxidations using Formic Acid and Hydrogen Peroxide *Proc Int Conf Polym Latex III 1989 London*
- 16 CAMPBELL, D S Unpublished Data Malaysian Rubber Producers' Research Association, United Kingdom
- 17 KOCHI, J K (1973) *Free Radicals* (Kochi J K ed), Vol 1, Chap 11 New York Wiley-Interscience
- 18 BARNARD, D, BATEMAN L, CUNNEEN, J I AND SMITH, J F (1963) *The Chemistry and Physics of Rubber-like Substances* (Bate-man L ed), Chap 17 London Maclaren
- 19 BARNARD, D AND LEWIS, P M (1988) *Natural Rubber Science and Technology* (Roberts A D ed), Chap 13 Oxford Oxford University Press
- 20 BOON, A J (1988) Hock Cleavage - The Cause of Main Chain Scission in Natural Rubber Autoxidation? *J nat Rubb Res* 3(2), 90
- 21 CHALK, A J AND SMITH, J F (1957) Catalysis of Cyclohexene Autoxidation by Trace Metals in Non-Polar Media Part I Metal Salts *Trans Farad Soc* 53, 1214
- 22 CHALK, A J AND SMITH, J F (1957) Catalysis of Cyclohexene Autoxidation by Trace Metals in Non-Polar Media Part 2 Metal Salts in the Presence of Chelating Agents *Trans Farad Soc*, 53, 1235
- 23 MAYO, F R, EGGER, K AND IRWIN, K C (1968) Accelerated Oxidations of Polyisoprene I Metal-catalysed Oxidations in Solution *Rubb Chem Technol*, 41, 271
- 24 BEVILACQUA, E M (1955) Chain Scission in the Oxidation of Hevea I *J Am Chem Soc* 77, 5394
- 25 BEVILACQUA, E M (1955) Chain Scission in the Oxidation of Hevea II *J Am Chem Soc*, 77, 5396
- 26 SOCIETE MERIDIONALE DU CAOUT-CHOUC SOMECA (1945) Manufacture of Plastified Rubber and Adhesive Latex *US Pat Appl No 2430481*
- 27 SHANLEY, E S AND GREENSPAN, F P (1947) Highly Concentrated Hydrogen Peroxide-physical and Chemical Properties *Ind Engng Chem*, 39, 1536
- 28 MERZ, J H AND WATERS, W A (1949) Some Oxidations involving the Free Hydroxyl Radical *J Chem Soc* S15
- 29 RAZUVAEV, G A AND BOGUSLAVSKAYA (1960) Syntheses by Means of Free Hydroxyl Radicals I Oxidative Dimerization of Aliphatic Ethers and Esters *J Gen Chem USSR (Engl Transl)*, 30, 4059
- 30 COTTON, F A AND WILKINSON, G (1972) *Advanced Inorganic Chemistry* 3rd edition, Chap 25 New York Interscience
- 31 VOGEL, A I (1961) *A Text Book of Quantitative Inorganic Analysis* 3rd edition, Chap 3 London Longmans
- 32 GREENSPAN, F P AND MacKELLAR, D G (1948) Analysis of Aliphatic Peracids *Analyt Chem* 20, 1061
- 33 CRITCHFIELD, F E (1963) *Organic Functional Analysis* Oxford Pergamon