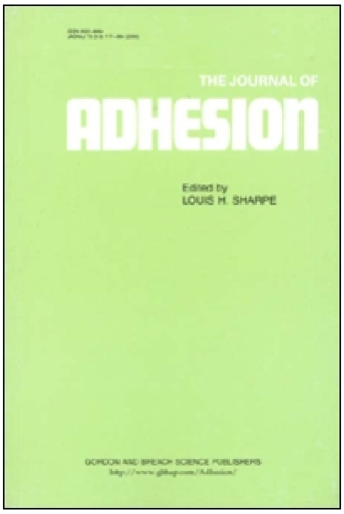

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Electrochemical Pretreatment of Polymers with Dilute Nitric Acid Either Alone or in the Presence of Silver Ions*

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X-ray Photoelectron spectroscopy (XPS) was used to detect major changes to the surface chemistry of polypropylene (PP), high density polyethylene (HDPE) and styrene-butadiene block copolymer (SBS) caused by electrochemical treatment using dilute nitric acid as electrolyte. Large increases in adhesion levels were observed with PP and HDPE. The method has the potential to be a commercial pretreatment that is inexpensive and safe. Further treatments were carried out in which the complex ion $(AgNO_3)^+$ was generated electrochemically. Effective pretreatment was achieved even with dilute solutions (0.001 M w.r.t. silver nitrate). Mechanisms are tentatively proposed for the electrochemical treatment when simply using an electrolyte of dilute nitric acid or where the anolyte consists of a solution of silver nitrate in dilute nitric acid.

Keywords: Electrochemical pretreatment; polymers; silver (II); oxidation; nitrate radical; XPS

1. INTRODUCTION

Many methods are available to pretreat polymers to enhance adhesion. The most important commercial methods for plastics are corona discharge [1–3], flame treatment [4–6], plasma treatment [7, 8]

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and, in the case of fully-fluorinated polymers, the use of sodium complexes [9 – 11]. These methods are not usually effective with elastomers where the use of various chlorinating agents, such as trichloroisocyanuric acid, is favoured [12, 13].

In 1997, details of a new electrochemical pretreatment were published [14]. The method involves the generation of the complex $AgNO_3^+$ ion by the anodic oxidation of silver nitrate in dilute nitric acid. Initial results were presented [14] showing that the treatment resulted in substantial improvements in adhesion with polypropylene (PP), plasticised poly(vinyl chloride), a styrene-butadiene block copolymer (SBS) and a fully-formulated vulcanised rubber (SBR). It was shown that the treatment was more effective, in terms of joint strength, with low-density polyethylene (LDPE) than with polypropylene [15]. It was also shown that the concentration of oxygen introduced into the PP surface was limited to about 4 atom%.

Treatment of a fully-formulated vulcanised rubber (SBR) demonstrated the etching nature of the treatment [16]. Analysis of an initial SBR surface by X-ray Photoelectron Spectroscopy (XPS) showed a material largely hydrocarbon in nature. Etching for one minute revealed substantial quantities of silicon, probably from the silica known to be in the formulation. Etching for 6 minutes revealed substantial quantities of aluminium as well as even higher concentrations of silicon; this is probably due to clay, also known to be in the formulation. The method is probably effective by reducing the concentration of any cohesively weak material from a surface and also by chemically modifying polymer surfaces. At least 10 atom percent oxygen was introduced into unformulated SBS and SBR systems [16].

A programme to study the mechanism of the electrochemical pretreatment is now in progress. A combination of techniques is being used in this study, including X-ray Photoelectron Spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS), adhesion measurements and gas chromatography mass spectrometry (GCMS). This paper describes the initial results of this programme in relation to the $(AgNO_3)^+$ complex ion. It also provides the first information on a new electrochemical treatment which uses only dilute nitric acid as the electrolyte.

2. EXPERIMENTAL

2.1. Materials

Silver nitrate and nitric acid were reagent grade materials obtained from Fisher Scientific. All solutions were made up in high purity millipore water of conductivity 18 MΩ.

Polyethylene (PE) films were prepared by hot pressing (140°C) additive-free, high-density polyethylene granules (Rigidex HD502XA, kindly supplied by BP Chemicals Limited) between additive-free polypropylene film or electropolished and anodised aluminium sheets kindly provided by Poeton Surface Treatments.

Styrene-butadiene-styrene (SBS) copolymer films were prepared in a similar way using granules of the polymer KRATON D-1102CU kindly supplied by Shell Chemicals. This polymer tended to adhere strongly to the separator materials used, especially polypropylene, from which it could not be separated. It could be removed with difficulty from aluminium or Melinex film by first cooling in liquid nitrogen. The film thickness varied from about 0.1 to 0.5 mm. The polypropylene film was blown by Venus Packaging from Neste VB 8050B homopolymer containing no additives other than processing stabilisers.

Araldite 2011A resin and 2011B hardener manufactured by Ciba-Geigy were mixed in small batches of 5 g of resin and 4 g of hardener. To assure a consistent glue line thickness, 1%, w/w, of ballotini spheres of 0.21 mm diameter were incorporated into the adhesive which was cured for 90 minutes at 60°C followed by 16 h at room temperature.

2.2. Apparatus and Procedures

2.2.1. Treatment of Small Molecules

Preliminary experiments on a number of model compounds including decane, decene, decanone, *tert*-butylbenzene, cumene and *n*-propylbenzene, supplied by Aldrich and used without further purification, were carried out with a view of determining the major oxidation products. The compound (1 ml) was added to a rapidly-stirred solution of the silver (II) complex generated from a 0.1 M solution of silver nitrate, which was prepared as described in the next section and left for two hours while the current was maintained at 500 mA. The resulting mixture was extracted with dichloromethane, washed with water, dried over sodium sulphate and submitted for GC-MS analysis using a 15 m JNW DB-5 MS capillary column and a Fisons MD 800 mass spectrometer. The major volatile products that could be identified are listed in Table I; these were identified by library matching except in the case of decane where a sample of 2-decanone was run.

An estimate was also made of the relative rates of oxidation of a number of compounds by the silver (II) species. The oxidant was generated as described above. The current was turned off and 0.1 ml of the test compound added to the rapidly-stirred solution. The potential of a platinum electrode was then recorded as a function of time *versus* a saturated calomel electrode connected to the cell *via* a sodium nitrate salt bridge. The silver (I)–silver (II) couple exhibits Nernstian behaviour, and the electrode potential, therefore, gives an indication of the amount of silver (II) left in the solution [17].

2.2.2. Treatment of Polymers with Electrochemically-generated Silver (II) Nitrate

The oxidising agent, $AgNO_3^+$, was generated by electrolysing a solution of 0.1, 0.01 or 0.001 M silver nitrate in 3.25 M nitric acid. 100 ml of this solution were placed in the anode compartment of a conventional two-compartment "H" cell. The catholyte, separated by a medium-porosity sintered glass frit, consisted of 3.25 M nitric acid. Small platinum spade or gauze electrodes were used at a current density of 200 mA cm^{-2}. The concentration of the dark brown silver complex appeared to reach a steady state after 10–15 minutes with no further change in the colour of the solution; measurement of the

TABLE I Major volatile products of the silver (II) oxidation of various model compounds

Compound	*Volatile products*
Decane	decanones
Decanone	not identified
n-Propylbenzene	propiophenone
Cumene	acetophenone
Tert-butylbenzene	tert-butyl *p*-benzoquinone

electrode potential showed that this also reached a steady state. Pieces of the polymer film typically 20 × 50 mm were then introduced at room temperature for various times as indicated in the results section. The films were washed in dilute nitric acid, rinsed in distilled water and dried at room temperature.

2.2.3. Electrochemical Treatment in the Absence of Silver Ions

Experiments were carried out to see if surface oxidation of hydrocarbon polymers can also be brought about by bringing the latter into direct contact with a platinum anode held at a potential of 2Vor more w. r. t. a saturated calomel electrode (SCE) in an electrolyte consisting of dilute nitric acid only. One method of achieving this is to rub gently a small platinum disc electrode over the polymer surface submerged below the surface 3.25 M nitric acid contained in a shallow dish provided with counter and reference electrodes (Pt disc method). This procedure is particularly suitable for the treatment of brittle materials such as polystyrene. A more convenient method, suitable for the treatment of relatively large, flexible polymer films, involves passage of the film over the edge of a platinum sheet anode partially masked with PTFE tape so as to leave an exposed edge approximately 0.5 × 1 × 47 mm using the same electrolyte, counter and reference electrodes as described above. The current (density) was adjusted manually, to maintain the anode potential in the range 2.1 – 2.9 V w.r.t. SCE. The film, typically 30 × 150 mm, was passed back and forth over the platinum edge typically 50 times for each side corresponding to a total contact time of five minutes; the actual treatment time for a given area of polymer is of the order of a few seconds. All experiments were carried out at room temperature.

2.3. Joint Strength Determination

Lap shear joints were prepared by bonding the polymer film between degreased, grit-blasted mild steel strips of dimension 60 × 20 × 3 mm with an overlap of 20 × 10 mm as shown in Figure 1. The adhesive was cured for 90 mins at 60°C followed by 16 h at room temperature (see Section 2.1).

FIGURE 1 Schematic diagram of lap shear test.

The joints were pulled apart on a Hounsfield HK50 tensometer at a crosshead speed of 10 mm min^{-1}. The failure load values quoted in the results section are average values from testing of four joints.

2.4. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was carried out on a VG Escalab Mk1 instrument using Al K_α X-rays. Quantification was achieved by measurements of peak areas after subtraction of a Shirley-type background, with appropriate corrections being made for photoelectron cross-sections, inelastic mean free paths, energy analyser transmission and angular asymmetry in photoemission.

3. RESULTS

3.1. Experiments with Small Molecules

The major volatile products of oxidation of a number of simple model compounds are listed in Table I. The change in the redox potential of the silver (I) – silver (II) system as a function of time for the addition of various compounds to a rapidly-stirred solution of electrochemically-produced silver (II) nitrate are shown in Figure 2.

3.2. Pretreatment of Polymers

The effect of the silver complex ion on the bondability of high-density polyethylene and polypropylene is shown in Figure 3. Corresponding XPS data showed maximum oxygen levels for HDPE and PP to be about 8 and 5 atom%, respectively. Treatment of SBS for five seconds using a 0.1 M silver nitrate solution introduced 10 atom% oxygen.

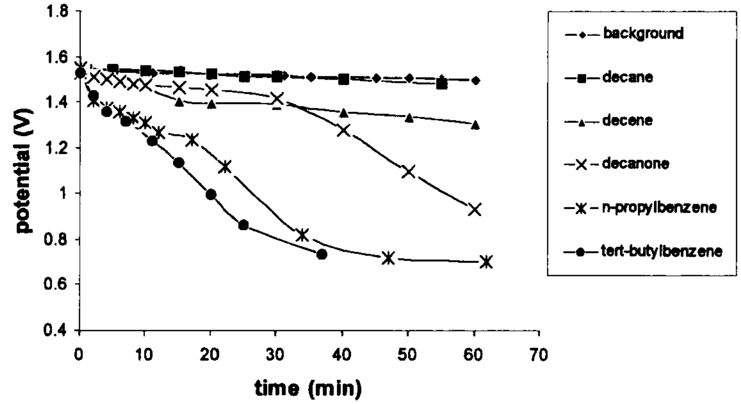


FIGURE 2 Potential (*vs.* SCE) as a function of time for the addition of various organic compounds to a solution of silver (II) nitrate.

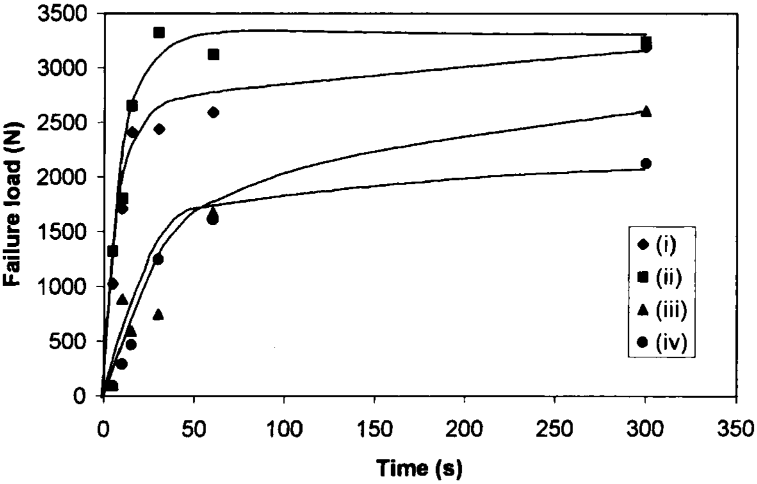


FIGURE 3 Failure load *versus* treatment time for the treatment of PP and HDPE at room temperature with silver (II) nitrate solutions. (i) HDPE 0.01 M $AgNO_3$, (ii) HDPE 0.1 M $AgNO_3$, (iii) PP 0.01 M $AgNO_3$, (iv) PP 0.1 M $AgNO_3$.

The corresponding results for polymers treated by direct contact with a platinum electrode, but in the absence of the silver complex ion, are given in Table II; the levels of oxygen introduced into the surfaces are, therefore, broadly similar for the two methods.

TABLE II Failure loads for the electrochemical treatment at room temperature of polymers in the absence of silver complex

		Surface composition atom %		
Polymer	*Treatment conditions*	*C*	*O*	*Failure load/N*
HDPE	No treatment	100.0	0.0	400
	2.1 V, Pt edge, 50 passes	95.5	4.5	1330
	2.4 V, Pt edge, 50 passes	96.2	3.8	1320
	2.9 V, Pt disc, 5 min	92.4	7.6	1110
PP	No treatment	100.0	0.0	0
	3.25 M nitric acid, 60 s	–	–	267
	2.1 V, Pt edge, 50 passes	92.6	7.4	2060
	2.4 V, Pt edge, 50 passes	93.1	6.9	2560
	2.9 V, Pt edge, 50 passes (H_2SO_4)	100	0	50
	2.9 V, Pt disc, 300 s, not touching	–	–	270
	2.9 V, Pt disc, 300 s, far removed	–	–	390
SBS	No treatment	100.0	0.0	–
	2.5 V, Pt edge, 50 passes	83.6	14.6*	–
PS	No treatment	100.0	0.0	550
	2.9 V, Pt disc, 300 s	94.5	5.5	670

* Cl 1.1%; Br 0.7%.

Notes.

a. All experiments were carried out in nitric acid (3.25 M) except where 10% sulphuric acid was used.

b. With failure loads up to 1 kN, the failure was apparent interfacial, above 2 kN it was cohesive within the polymeric substrate and between 1–2 kN, the failure was of mixed mode.

c. Failure loads are not recorded for SBS because of the low cohesive strength of copolymer.

4. DISCUSSION

4.1. Treatment with Silver Complex

A number of interesting observations may be made from the results in Figure 3 and those described in the Introduction. The concentration of silver nitrate does not appear to have an important effect on bondability. The oxygen concentration after treatment of PP was limited to about 4–5 atom% both in the earlier [15] and the present study. This is in line with a study of chromic acid treatment of polyolefins [18]. With PP, the oxygen concentration was limited to about 5 atom%, whereas, with LDPE, the concentration of oxygen after the same treatment was much higher. The limited concentration in the case of PP was attributed to chain scission and the same explanation is likely with the electrochemical pretreatment.

The results obtained with SBS are of particular interest. Treatment with a 0.1 M solution of silver nitrate at room temperature for only five seconds resulted in a surface concentration of oxygen of 10 atom% and the same level of oxygen was introduced into polystyrene after 60 seconds. This suggests that the presence of aromatic and/or alkenic moieties in a hydrocarbon polymer results in an increase in reactivity towards the silver (II) oxidising agent. It is tempting to ascribe this to the presence of benzylic and/or allylic groups but the situation is clearly more complex, since both *n*-propylbenzene and *tert*-butylbenzene react at about the same rate and much more rapidly than the saturated hydrocarbons (see Fig. 2). Analysis of the reaction products shows the expected product, propiophenone, arising from attack at the benzylic position of *n*-propylbenzene. Blocking of the benzylic position as in *tert*-butylbenzene results in attack at the aromatic ring to yield the corresponding benzoquinone (see Tab. I). Addition of 2-decene or 2-decanone to a silver (II) solution also results in rapid discharge of the characteristic dark brown colour but the fall in potential is much less pronounced. Addition of saturated hydrocarbons such as pentadecane, decane or heptane have no effect on the colour and the potential-time curve is barely distinguishable from the background curve.

4.2. Electrochemical Treatment in Absence of Silver Complex

Paire *et al.* [19] have shown that silver (II) nitrate produced by the reaction of silver (II) oxide with nitric acid is not capable of oxidising straight chain alkanes such as dodecane. They showed that oxidation occurs at a measurable rate only in the presence of a polarised anode and nitric acid and put forward the suggestion that the oxidation is initiated by anodically-generated nitrate radicals ($NO_3^{\bullet}$). Tomat had suggested earlier that these species are involved in the electrochemical oxidation of aliphatic hydrocarbons in oxygen-saturated *t*-butanol-nitric acid mixtures to yield mixtures of the corresponding isomeric ketones [20]. The key step in the oxidation involves hydrogen atom abstraction or electron transfer by, or to, the highly reactive nitrate radical [21]. In the present study, in an attempt to test this hypothesis, experiments were carried out where the anode was brought into intimate contact with the polymer surface so that nitrate radicals generated at the anode by the reaction

$$NO_3^- \longrightarrow NO_3^{\bullet} + e \quad E = 1.8\,V \; vs.\; SCE$$

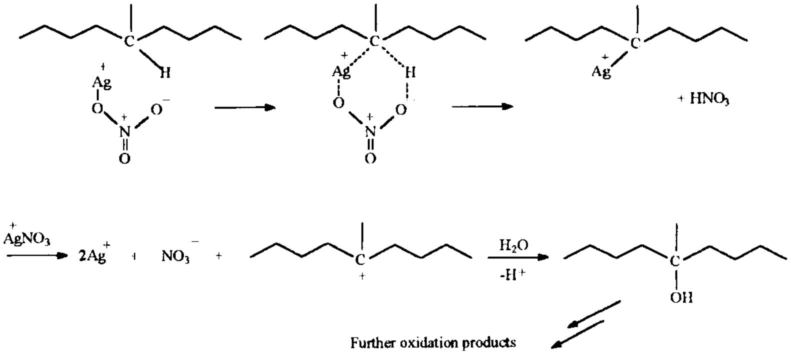
could react with the polymer before they became deactivated by reaction with the electrolyte. Examination of the XPS and failure load data presented in Table II clearly shows that oxidation of the polymers had indeed taken place. The effect appears to be most pronounced for SBS with respect to chemical modification and with PP in terms of bond strengths. The treatment was less effective for the oxidation of HDPE where bond strengths were lower by a factor of two compared with the values observed for PP. Treatment of SBS resulted in a relatively highly oxidised surface containing up to 15% oxygen. Further support for the involvement of nitrate radicals is provided by the observation that no oxygen is incorporated into polypropylene when the nitric acid is replaced by sulphuric acid.

4.3. Mechanisms of the Two Electrochemical Treatments

Satisfactory mechanisms should account for: (i) the introduction of substantial quantities of oxygen into polyolefins with both electrochemical treatments, (ii) the higher joint strengths of PE compared with PP for the silver (II) mediated reaction after a given treatment time and (iii) the greater extent of PP oxidation compared with PE for the nitrate radical mediated process.

We suggest tentatively that the key step in the oxidation of the polymer proceeds by attack of the silver (II) complex on a carbon hydrogen bond to yield initially the alcohol which is, however, rapidly oxidised to yield carbonyl groups and possibly other products arising from further oxidative chain scission as shown in Scheme 1; it has been shown in a separate experiment that alcohols react much more rapidly than saturated alkanes with the AgII complex.

This mechanism is sterically very demanding and attack on the relatively accessible methylene hydrogens in HDPE should be favoured over those in the more hindered PP.



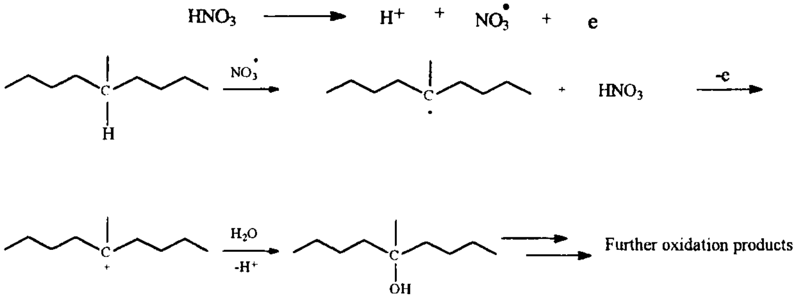
SCHEME 1 Proposed mechanism for the reaction of silver complex with polyolefins.

According to Paire [19], aliphatic hydrocarbons such as dodecane are not oxidised by solutions of the silver (II) nitrate complex produced chemically by the action of nitric acid on silver (II) oxide. We, too, were unable to detect oxidation products when liquid alkanes were treated with electrochemically-generated silver (II) nitrate in the absence of a polarised anode. It is, therefore, somewhat surprising to find that the surfaces of both HDPE and PP are readily oxidised by the silver (II) species, with the former apparently exhibiting somewhat higher reactivity than the latter. Chain scission may be greater in the case of PP and this would limit the degree of oxidation detected by XPS. Even for silver concentrations as low as 0.001 M, significant increases in the oxygen levels and failure loads were observed. With polymers, the oxidation products are concentrated within the surface regions and are therefore amenable to detection by XPS. On the other hand, the detection limits of the GC-MS system were insufficient to detect the presence of oxidised species. This will be partly due to the fact that the oxidation products are more reactive than the starting hydrocarbons; the reactants are, in fact, ultimately broken down to carbon dioxide and water.

Another feature of the treatment that requires an explanation is the observation that the amount of oxygen that can be introduced into the surface of HDPE and PP is relatively small, reaching a limiting value of less than 10 atom percent for prolonged treatment times. This may be due to chain scission either as a consequence of the initial oxidation or brought about by further oxidation of the polymer once functionalised. The results presented in Figure 2 show that functionalised compounds are oxidised much more readily than the parent alkanes and do not require the presence of the polarised anode. It appears that once the polymer has been functionalised further oxidation proceeds rapidly by further reaction at the functional group, resulting ultimately in complete mineralisation of the organic species [19]. Arenes and alkenes are also readily oxidised, which would account for the relatively large oxygen uptake by unsaturated and aromatic polymers such as SBS and PS. It is unclear why there was no substantial increase in joint strength with PS after treatment.

The oxidation of the polyolefins in direct contact with the anode (and in the absence of silver ion) is unlikely to proceed by direct electron transfer from the hydrocarbon to the anode. Such reactions take place at very high potentials requiring the use of nonaqeous solvents and/or extremely acidic conditions such as those encountered in solutions of the so-called super acids [22]. The oxidation requires a nitric acid medium as no oxygen is introduced when sulphuric acid is used instead. It is, therefore, reasonable to assume that a reactive species produced as a result of the anodic oxidation of nitric acid is responsible for the actual oxidation of the polymers. According to Tomat [20], nitric acid is readily oxidised at potentials in the region of 2 V *vs.* SCE to generate highly-reactive, short-lived nitrate radicals. These are capable of initiating oxidation by abstraction of hydrogen atoms from the polymer. Such a process is likely to be sterically far less demanding than the concerted mechanism suggested for attack by the silver (II) complex. No nitrogen is observed in the treated polymers using XPS; reaction between polymer radicals and nitrate is, therefore, unlikely. In addition, the nitrate radical may exhibit a degree of selectivity towards the more reactive tertiary hydrogen atoms of PP, producing a more highly oxidised surface under a given set of conditions and this results in the much greater failure loads for PP when compared with HDPE (Tab. II). Scheme 2 is, therefore, put forward tentatively for the direct electrochemical surface modification of polyolefins:

This mechanism is similar to that proposed by Tomat [20] for the anodic oxidation of alkanes, in that the key step is the abstraction of a hydrogen atom by the nitrate radical but it does not require the presence of molecular oxygen for the formation of the final product. It is difficult to establish the involvement of oxygen in our case because



SCHEME 2 Proposed mechanism for the reaction of nitrate radicals with polyolefins.

this gas is evolved continuously at the potentials used in this work. The oxidation of the radical intermediate may proceed by electron transfer to the nitrate radical or, if adsorbed species are involved, directly to the electrode. The question as to whether solution free or adsorbed nitrate radicals are involved has yet to be determined.

5. CONCLUSIONS

- It has been shown that electrochemically-generated silver (II) nitrate is an effective oxidant for the pretreatment of a number of hydrocarbon polymers even when generated from very dilute (*e.g.*, 0.001 M) silver nitrate solutions.
- Experiments involving direct contact between a polarised anode and the polymer surface show that effective pretreatment can be achieved in the absence of silver ions.

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