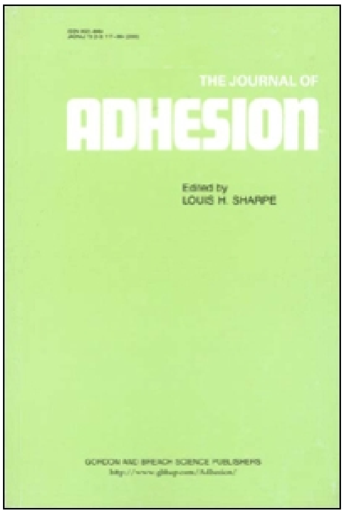

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The Reduction in Contact Adhesion of Some Adhesives for Paper by Treatment with Zirconium Chemicals

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The Reduction in Contact Adhesion of Some Adhesives for Paper by Treatment with Zirconium Chemicals†

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Reclamation of paper is a very important industry in the UK and in many other countries. However, the adhesives used with the original paper make successful reclamation much more difficult due to the formation of tacky particles called "stickies". This paper describes the use of zirconium compounds to ameliorate this problem.

INTRODUCTION

In 1985, the net imports of paper and board into the UK were worth many hundreds of millions of pounds. This figure would have

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been substantially greater if waste paper was not recycled. However, the adhesives present in waste paper (labels, envelope seals, book binding adhesives, etc.) limit the quantity of paper that can be recycled economically and also adversely affect the quality of the reclaimed fibre. During the reclamation process, adhesive particles termed "stickies" cause various problems. In particular, they:

i) Adhere to the processing equipment and must be removed periodically

ii) Bond to the fibres; this can cause subsequent processing difficulties and also lead to unsightly spots in the paper produced.

The contaminants which are responsible for the formation of the majority of stickies[1,2,3] are hot melt (HM), pressure sensitive (PS) and hot melt pressure sensitive (HMPS) adhesives. Typical adhesives used in the paper industry are listed in references 2 to 6.

Tackifying resins used in the HM, PS, and HMPS adhesives may also present problems. Examples are wood rosin and rosin esters, polyterpene resins, and aliphatic and aromatic hydrocarbon resins.

The stickies problem may be aggravated by the conditions used during the pulping process in a paper mill. The temperature may be increased to greater than 50°C and pH may vary between 3 and 10. Also, significant amounts of calcium may be present in the pulp. In particular, high pH conditions have been held responsible for rendering sticky particles even more tacky. Stickies are difficult to remove completely by physical separation because they are of similar size and density to pulp fibres.

A promising approach to reduce the problems of stickies has been the incorporation of zirconium chemicals during the repulping process. Tests in paper mills and laboratories[7] have shown that zirconium chemicals significantly reduce the tackiness of the stickies. Zirconium has a strong affinity for oxygenated species;[8] for example, oxygenated groups on organic polymers can interact with zirconium species. Thus the mechanism by which the tackiness of the stickies is reduced may involve reaction of zirconium chemicals with functional groups such as carboxyl and hydroxyl on the surfaces of the adhesive contaminants.[7] This may result in the formation of a layer of zirconium compounds on the sticky surface which renders it less tacky.

The aims of this study were to obtain quantitative data on any reduction in adhesion after treatment of adhesives with zirconium solutions, investigate the effect of high pH solutions on adhesion and examine whether or not zirconium chemicals migrate into the adhesives.

A test was devised to simulate the adhesion of the adhesives to the processing machinery before and after treatment with zirconium chemicals. The distribution of zirconium chemicals between the adhesives and water was investigated using a permeation technique. X-ray photoelectron spectroscopy (XPS) was used to examine the surfaces of the adhesives after treatment with a zirconium chemical.

MATERIALS

Adhesives

Adhesives A to H, which are typical of those used in the paper industry,[3] were supplied by Croda Adhesives Ltd and are described below. Adhesive J, also supplied by Croda, was specially prepared to provide an adhesive which would be relatively chemically inert.

A) A pressure-sensitive (PS) acrylic dispersion containing mainly butyl acrylate with some 2-ethyl hexyl acrylate. Adhesive A probably contains carboxylic acid groups.

B) This is a dispersion of a high molecular weight VAE copolymer containing about 20% ethylene, 7% dibutylphthalate and an anionic surfactant.

C) A dispersion of medium molecular weight vinyl acetate polymer containing 5% added low molecular weight 88% hydrolysed poly (vinyl alcohol), 8% dibutylphthalate, and a non-ionic surfactant.

D) This hot-melt (HM) adhesive is based on an EVA copolymer (20–28% VA), a rosin ester (pentaerythritol), and a paraffin wax of melting point 155°C. The ratio of copolymer:rosin ester:wax is approximately 1:1:1. Butylated hydroxytoluene (BHT) is present as an antioxidant (0.2%).

E) A pressure-sensitive hot-melt (PSHM) adhesive which is a blend of an EVA copolymer with a poly-l-methyl styrene resin (40%) and a rosin derivative (30%). An antioxidant is also present.

F) This PSHM adhesive contains a styrene-butadiene-styrene (SBS) block copolymer (30%) and a mixture of high and low melting point rosin esters. Also present are antioxidants Wingstay L and Polygard.

G) A remoistenable HM adhesive containing a polyvinylpyrrolidone (60%)—ethylene vinyl acetate copolymer (40%), wax and rosin.

H) This is a uv-resistant, acrylic-based PSHM adhesive.

J) This is a modified form of adhesive F in which the rosin derivatives have been replaced by a solid and liquid hydrogenated hydrocarbon resin.

Zirconium Compounds

The following zirconium chemicals were supplied as aqueous solutions by Magnesium Elektron Ltd: zirconium acetate and Bacote 20† which is a stablised form of ammonium zirconium carbonate.

Buffer Solutions

Two buffer solutions were used: pH10 prepared from BDH Convol vials containing boric acid, potassium chloride and sodium hydroxide, and pH12 prepared from May and Baker Volucon buffer concentrate containing glycine, sodium chloride and sodium hydroxide.

EXPERIMENTAL

Permeation Studies

Thin films of adhesives which are free from pinholes are needed for permeation experiments. Initially, attempts were made to produce thin films from the solid adhesive samples (D, E, F, G and H) for

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† Tradename of Magnesium Elektron Ltd.

use in permeation cells. Films were prepared between two PTFE sheets using a small hydraulic press. Temperature and pressure were varied to control film thickness; however, films of adhesives E, F and H were extremely sticky and could not be removed from the PTFE sheets. Also, films of adhesive G were found to be very brittle and could not be removed intact from the PTFE. Thus, this method was only applicable to adhesive D, where films 0.1 mm to 0.2 mm thick could be made by applying a pressure of 5 MNm^{-2} for half a minute at 100°C. The films produced did not contain pin holes and were suitable for use in permeation cells.

Films of adhesives C, E and G were prepared on or between silicone release paper (Stera-Lease, Sterling Coated Materials Ltd). Adhesive C was brushed on to silicone release paper and left to dry; it could then easily be removed. Films of adhesives E and G were prepared by pressing between silicone release paper in the hydraulic press using a pressure of 3 to 5 MNm^{-2} and a temperature of 110 to 130°C. Although the films could be removed fairly easily from the release paper, they were very difficult to handle because of the very tacky nature of adhesive E and the brittleness of adhesive G, and could not be used.

To avoid these problems, films of adhesives E, F, G and H were prepared by pressing between two sheets of filter paper in the hydraulic press using a pressure of 5 MNm^{-2} and temperatures between 100 and 200°C. Films of adhesives A and B were brushed onto filter paper and left to dry. These adhesive-filter paper composite films were very easy to handle and could be satisfactorily used in preparing permeation cells.

Film thicknesses were measured at 10–12 points using a micrometer. Permeation cells were made by bonding discs of adhesive films onto one end of a glass tube, 30 mm in diameter and approximately 120 mm long, using adhesive D. (Later results show adhesive D is impermeable to zirconium compounds). The tubes were partially filled with 10 cm^3 of zirconium acetate solution (1% ZrO_2) and placed in beakers containing magnetically stirred deionised water so that the liquid levels inside and outside the tubes were the same (Figure 1). These were stored at room temperature and at various time intervals a 10 cm^3 sample of deionised water was removed for zirconium analysis by a method based on that of Mayer and Bradshaw.[9]

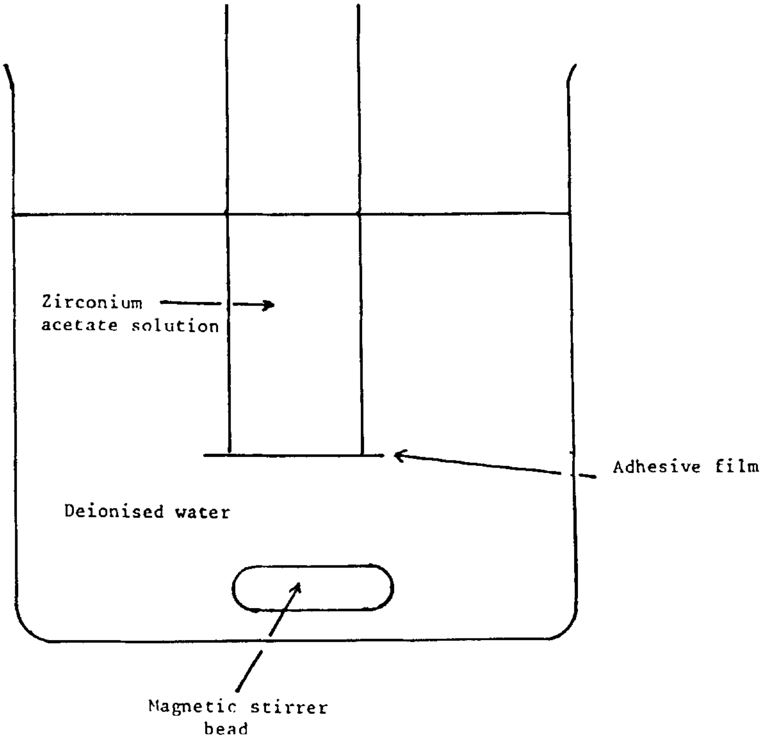


FIGURE 1 Permeation cell.

Adhesion Measurements

Glass plates 65 mm square were cleaned in chromic acid (7 parts by weight potassium dichromate, 12 parts water, 150 parts concentrated sulphuric acid) at room temperature for 20 minutes, rinsed in running tap water for 20 minutes and dried in an oven at 60–65°C for 30 minutes. The dispersion adhesive A was spread on the glass plates and left to dry at room temperature for three days. The hot melt and pressure-sensitive hot melt adhesives (D, E, F, J) were melted onto glass plates by heating in an oven at 140°C for 45 minutes. To measure adhesion, a mild steel cylinder was placed on the adhesive and a 509.5 g weight was placed on top (to give a force of 50 N). The weight was removed after one minute and the force required to remove the cylinder was then measured using an Instron

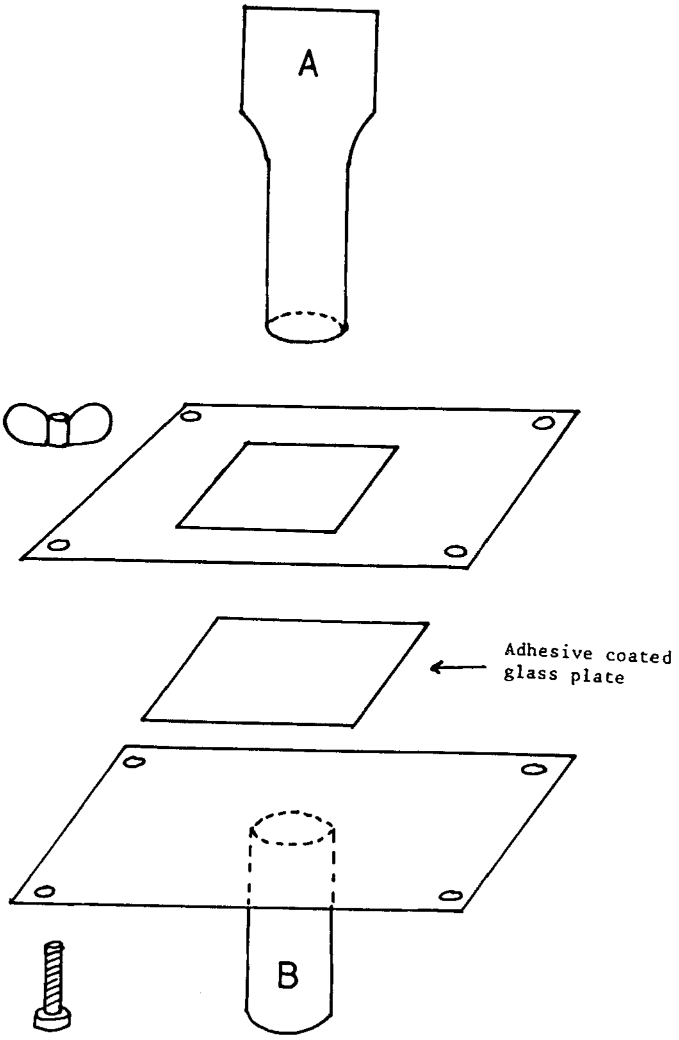


FIGURE 2 Adhesion testing jig. The mild steel plates bolt together to hold the glass plate, and parts A and B are clamped into the Instron.

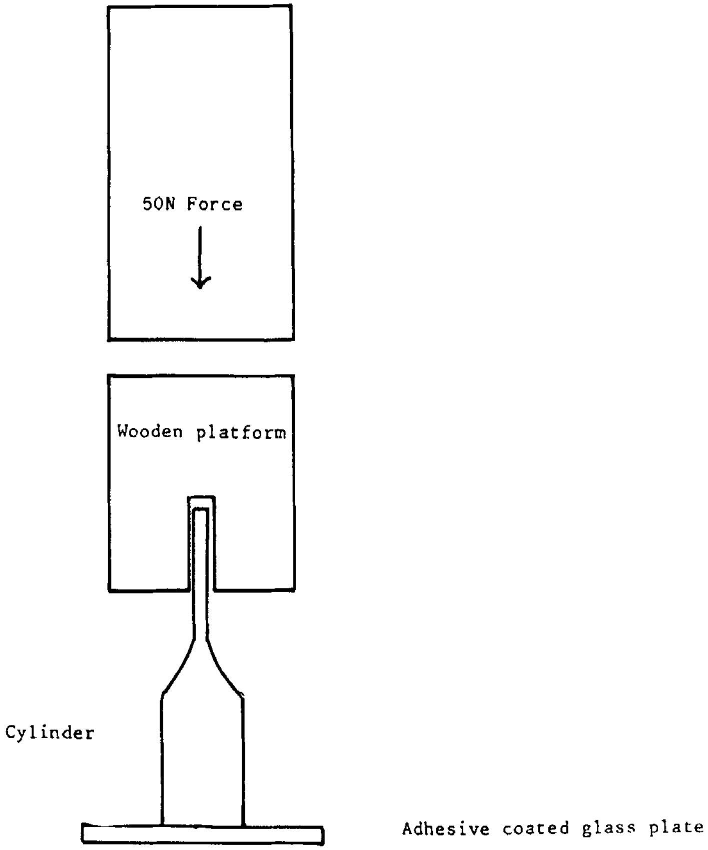


FIGURE 3 The application of pressure to an adhesive.

1026 mechanical testing instrument with a crosshead speed of 100 mm $\min^{-1}$. A specially constructed jig permitted the glass plates to be attached to the Instron 1026, as shown in Figure 2. After each measurement, the cylinder was wiped three times with tissue paper soaked in acetone, dipped in clean acetone and left to dry. The diameter of the cylinder was 25 mm and its weight 224.9 g. The weight of a wooden platform which enabled the 50 N force to be applied on the cylinder (Figure 3) was 164.2 g, hence the total force at the base of the cylinder was 53.9 N.

Adhesion was measured either before or after immersion in various solutions of zirconium acetate, Bacote 20 or buffer solutions. These treatements were compared with the effect of immersion in de-ionized water or acetic acid the solutions of which had pH adjusted to match those of the zirconium acetate solutions.

Before testing, surplus liquid was removed by shaking three times. Five samples were used for each experimental condition. Where treatments involved more than one solution, samples were immersed in each solution for 30 minutes. For very dilute (20 ppm) zirconium solutions infinite (i.e., 1 litre per sample) stirred baths were used.

Adhesives C and G were not tested as permeation experiments showed them to be partially soluble in aqueous solutions.

Tack Measurements

The tack of adhesives E and F was measured using the Instron and the jig described above. Adhesive samples were prepared in the usual way and clamped in the lower jaws of the Instron. The mild steel cylinder was clamped in the upper jaws and lowered onto an adhesive sample at a crosshead speed of 100 mm min^{-1}. However, immediately the Instron registered contact between the cylinder and an adhesive sample, the cylinder was raised. The force required to separate the cylinder from the adhesive was measured, and for adhesive F, the tack was also measured after treatment with zirconium acetate solution (1% ZrO_2).

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Films of the adhesives were prepared on substrates of poly(ethyleneterephthalate) film. Adhesives A, B and C were spread on the film and left to dry for 3 days. Adhesives D to J were melted on the film by heating for 45 minutes at 140°C. Samples of adhesives A to H were placed in zirconium acetate solution (1% ZrO_2) for 30 minutes, the excess liquid being removed by shaking the samples 3 times. The samples were then rinsed twice with deionised water and dried in a desiccator. After drying, pieces approximately 10 mm square were cut from each sample. An unheated sample of adhesive J was also prepared. XPS spectra were obtained using an ESCALAB Mark 1 spectrometer, equipped with a VGS 1000 Apple computer based data acquisition system and an AG 21 Argon ion gun. Spectra were recorded of the as-received surfaces and in order to investigate the diffusion of zirconium into the films, spectra were also recorded following 1 and 10 minutes argon ion etching. 3 keV Argon ions focused by 1.5 keV on the focusing ring were used to etch the samples. High-resolution spectra were recorded of the Zr(3d), C(1s) and O(1s) peaks and any other elemental peaks identified in low resolution survey spectra. Aluminium Kα X-rays were used throughout and the analyser pass energy was set at 50 eV to record survey spectra and 20 eV to record high resolution spectra.

Integrated counts above a linear background were taken as the measure of peak intensities and quantification factors[10] were used to convert the intensity data to atomic percentages. No corrections were made for differences between analyser transmission functions of the ESCALAB spectrometer and the instruments used to obtain the quantification factors. Surface carbon peaks were split into the COH, COOH and CH components by manually fitting three mixed Gaussian-Lorentzian curves to the data.

RESULTS

Permeation Studies

For adhesives A, B, D, E, F and H no detectable zirconium permeation occurred after 9, 7, 9, 24, 28 and 7 days respectively.

Permeation was observed for adhesive G; however, at the end of the experiment, only a white powdery deposit remained between the filter papers, indicating that part of the film had dissolved. Adhesive C which contains poly(vinyl alcohol) dissolved in the solutions.

Adhesion Measurements

The adhesion results on adhesives A, D, E, F, H and J are presented in Tables I to VII. Errors shown are standard deviations. Treatment time is 30 minutes except where specified as 24 hours.

TABLE I
Adhesion measurements for adhesive A

Treatment	Concentration	pH	Adhesion (N)	Reduction in adhesion (%)
Untreated			264 ± 2	
Deionised water			73 ± 9	72
Zirconium acetate[a]	20 ppm	7.0	14 ± 7	93
Bacote 20	20 ppm	6.9	69 ± 20	74
Acetic acid	0.0003%	5.0	67 ± 10	75
Zirconium acetate	20 ppm	5.0	23 ± 6	91
Zirconium acetate (24 hrs)	20 ppm	5.0	0	100
Acetic acid	0.02%	3.8	50 ± 10	83
Zirconium acetate	1% ZrO_2	3.8	3 ± 1	99
Buffer solution		12	0	100
Buffer solution[b]		12→7	6 ± 5	98
Buffer solution with 250 ppm Ca[c]		12→7	18 ± 5	93

[a] The pH of this solution was increased from its natural pH of 5.0 by adding sodium acetate buffer solution (prepared by adding 75 cm^3 0.01 M acetic acid to 100 cm^3 sodium acetate).

[b] Dilute hydrochloric acid was added to reduce the pH from 12 to 7.

[c] After treatment at pH 12, Ca was added in the form of $CaCl_2$ followed by dilute hydrochloric acid to reduce the pH to 7.

Adhesive B was only slightly tacky when untreated (having an adhesion value of 0.6 ± 0.5 N) and had no measurable adhesion once immersed in deionised water or zirconium acetate.

Adhesive C dissolved in the solutions and therefore its adhesion was not measured.

TABLE II
Adhesion measurements for adhesive D

Treatment	Concentration	pH	Adhesion (N)	Reduction in Adhesion (%)
Untreated			236 ± 56	
Deionised water			220 ± 56	7
Bacote 20	20 ppm	6.9	63 ± 24	73
Acetic acid	0.0003%	5.0	166 ± 80	30
Zirconium acetate	20 ppm	5.0	7 ± 7	97
Acetic acid	0.02%	3.8	95 ± 25	60
Zirconium acetate	1% ZrO_2	3.8	0	100
Buffer solution		12	0	100

TABLE III
Adhesion measurements for adhesive E

Treatment	Concentration	pH	Adhesion (N)	Reduction in adhesion (%)
Untreated			295 ± 49	
Deionised water			250 ± 11	15
Bacote 20	20 ppm	6.9	136 ± 28	54
Acetic acid	0.0003%	5.0	177 ± 72	40
Zirconium acetate	20 ppm	5.0	108 ± 34	64
Zirconium acetate (24 hrs)	20 ppm	5.0	119 ± 16	60
Acetic acid	0.02%	3.8	132 ± 26	55
Zirconium acetate	1% ZrO_2	3.8	39 ± 9	87
Buffer solution		10	175 ± 47	41
Buffer solution[a]		10→8	227 ± 61	23
Buffer solution with 250 ppm Ca[b]		10→8	39 ± 14	87

[a] The pH was reduced to 8 by adding dilute sulphuric acid.

[b] After reducing the pH to 8 as above, samples were treated with zirconium acetate solution.

TABLE IV
Adhesion measurements for adhesive F

Treatment	Concentration	pH	Adhesion (N)	Reduction in adhesion (%)
Untreated			360 ± 8	
Deionised water			310 ± 8	−14
Bacote 20	20 ppm	6.9	395 ± 50	−10
Acetic acid	0.0003%	5.0	397 ± 25	−10
Zirconium acetate	20 ppm	5.0	251 ± 36	30
Acetic acid (24 hrs)	0.0003%	5.0	447 ± 64	−24
Zirconium acetate (24 hrs)	20 ppm	5.0	430 ± 52	−24
Acetic acid	0.02%	3.8	290 ± 49	19
Zirconium acetate	1% ZrO_2	3.8	41 ± 24	89
Buffer solution		10	282 ± 63	22
Buffer solution		12	140 ± 20	61

TABLE V
Adhesion measurements for adhesive H

Treatment	Concentration	pH	Adhesion (N)	Reduction in adhesion (%)
Untreated			314 ± 22	
Deionised water			38 ± 6	88
Zirconium acetate	1% ZrO_2	3.8	4 ± 2	99

TABLE VI
Adhesion measurements for adhesive J

Treatment	Concentration	pH	Adhesion (N)	Reduction in adhesion (%)
Untreated			222 ± 38	
Acetic Acid	0.2%	3.8	118 ± 8	47
Zirconium Acetate	1% ZrO_2	3.8	44 ± 11	80

TABLE VII
Tack measurements

Adhesive	Treatment	Mean tack (N)
E	Untreated	4 ± 4
F	Untreated	202 ± 89
F	Zirconium Acetate (1% ZrO_2; pH 3.8)	2 ± 1

TABLE VIII
XPS analysis of zirconium acetate treated adhesives

	Atomic concentration (%)				
Adhesive	Zr	C(C – H)	C(C – O)	C(C – COO)	O
A	0.9	57.2	13.6	7.2	21.1
B	0.7	42.4	20.5	9.0	27.0
C	3.5	39.5	16.2	5.2	35.6
D	1.1	80.5	—	4.7	13.8
E	0.4	94.8	—	—	4.8
F	1.4	86.5	—	—	12.2
G	1.6	77.5	—	5.8	15.1
H	0.8	59.7	9.9	8.4	21.2

TABLE IX
XPS analysis showing the variation of Zr concentration with etching time

Ar$^+$ Etch time/min Adhesive	0	1	10
	Atomic % Zr		
A	0.9	1.7	1.3
B	0.7	0.9	0.5
C	3.5	0.5	0.9[2]
D	1.1	1.2	0.2
E	0.4	0.5	0.3
F	1.4	1.8	0.9
G	1.6	1.2	1.1
H	0.8	1.2	0.5

[a] 12 minute etch.

Adhesive D was non-tacky at room temperature, but showed good adhesion at 70°C. Thus all treatments for adhesive D were carried out at 70°C. For the remaining adhesives, measurements were taken under ambient conditions.

XPS Analysis

XPS analyses of adhesive surfaces treated with zirconium acetate solutions are shown in Table VIII. Table IX shows the results of argon ion etching which indicate zirconium concentration depth profiles. XPS analysis of adhesive J showed the presence of functional groups both before and after heating, despite the hydrocarbon composition of this adhesive.

DISCUSSION

Permeation Studies

The results of the permeation studies show that zirconium acetate does not permeate through films of adhesives A, B, D, E, F, and H. Films of adhesive C are water soluble[11] and are therefore not suitable for permeation work.

Adhesive G is a water-sensitive, remoistenable hot melt used for envelope flaps,[12] and, as already mentioned, only a white powdery deposit remained between the filter papers at the end of the experiment, indicating that adhesive G had partially dissolved in the zirconium acetate solution.

Adhesion Measurements

Adhesion measurements were not made for adhesives C and G due to their high solubility in aqueous solutions. Adhesive B was only slightly tacky when untreated and had no measureable adhesion after immersion in deionised water or zirconium acetate. Thus most of the work was concentrated on adhesives A, D, E and F, these being representative of the adhesives most likely to cause sticky problems in a paper mill.

Treatment of the adhesives by zirconium acetate was first investigated at a 1% level and was found to be very effective for all the adhesives, reducing adhesion by between 80% and 100%. However, when the concentration of zirconium acetate was reduced to 20 ppm, which is the level of addition recommended for use in paper mills, differences in the behaviour of the adhesives towards zirconium acetate became apparent. At this lower level of addition, adhesion was still effectively reduced for adhesives A and D, but the effect was much less pronounced for adhesive E even after 24 hours. For adhesive F, adhesion was reduced by only 30% and after 24 hours, adhesion increased by 19%. However, in all cases treatment with zirconium acetate reduced adhesion to a greater extent than treatment with the corresponding acetic acid blank solutions. When the pH of 20 ppm zirconium acetate solution was increased to pH 7, the reduction in adhesion for adhesive A was not significantly different from that produced by 20 ppm zirconium acetate solution at its natural pH of 5.

The results for treatment of adhesives by Bacote 20 show that this zirconium solution is not as effective in reducing adhesion as zirconium acetate solution. Treatment of adhesive F again produced an increase in adhesion, this time after only 30 minutes.

Generally, treatment of an adhesive with a blank solution produced a decrease in adhesion which was noticeably less than that produced by treatment with a zirconium chemical. Deionised water had the greatest effect on the acrylic adhesives A and H reducing adhesion by 72% and 88%, respectively. For the remaining adhesives, the reduction in adhesion was comparatively small; up to 15%. Similarly, acetic acid had the largest effect on adhesive A and only a moderate effect on adhesives D, E and J. For adhesive F, pH5 acetic acid actually increased adhesion and this increase was larger after 24 hours.

Treatment of adhesives with buffer solution at pH 10 produced decreases in adhesion in each case, although these decreases were smaller than those observed for 20 ppm zirconium acetate solutions. When the pH was lowered from 10 to 8, there was no significant change in adhesion. For adhesives A and D at pH 12, adhesion was reduced to zero. This is probably due to the adhesive surface being hydrolysed. Thus a solution to the stickies problem would appear to be to run the repulping process at pH 12. However, in practice, it is not possible to pulp at such a high pH.

Adhesion was observed to increase slightly for adhesive A when the pH was lowered from 12 to 7, particularly in the presence of calcium. Acrylic adhesives such as A are surfactant stabilised and it is possible that calcium may complex with the surfactant and precipitate it out leaving the adhesive more tacky. However, it is unlikely than the small observed increase in adhesion in the presence of calcium for adhesive A would cause problems in the paper mill. Other workers have observed much larger increases in adhesion.[13]

To summarise; zirconium compounds reduced the adhesion of all the adhesives studied. Treatment was more effective for the acrylic and EVA adhesives (A, D and E) than for the SBS adhesive, F. Treatment of adhesive F was most effective after short immersion times. The reductions in adhesion mean that the adhesives are much less likely to adhere to the processing machinery in a paper mill.

Tack Measurements

The tack measurements for untreated adhesives E and F (Table VII) were much lower that the corresponding adhesion measurements, particularly for adhesive E. The tack of untreated adhesive E was too low to allow this adhesive to be used in further contact tests. Treatment of adhesive F with 1% zirconium acetate solution reduced tack by 99%; the corresponding reduction in adhesion was 89%.

XPS Analysis

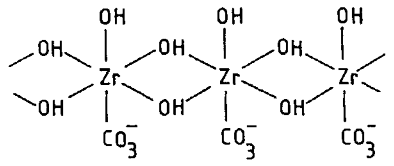
XPS analyses of adhesives treated with zirconium acetate solutions (Table VIII) show that zirconium is present in the surfaces of all eight adhesives. Adhesive C, which is water soluble, absorbs the largest amount of zirconium and entry here was probably into a highly water-swollen polymer.

Observation of zirconium following argon etching of the surfaces indicates that zirconium compounds have penetrated into the adhesive films or have deposited on the adhesive surfaces in the form of islands. It is not possible to estimate the mean thickness of the islands or the depth of penetration of the zirconium into the film because the initial etch rates and the effects of graphitisation on the etch rates of the adhesives are not known. In addition, when organic materials are associated with heavy metals, selective sputtering of the polymer can occur[14] which results in a surface that is relatively rich in metal. In all cases (except for adhesive C which is water soluble) zirconium levels decrease following more than 1 minute of argon etching and this is consistent with the concentration of zirconium in surface regions of the film or of the presence of relatively thin islands of deposited zirconium compounds on the adhesive surface. This is in accord with the observation that no permeation of zirconium acetate through films of the adhesives was detected.

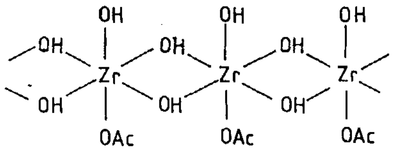
Mechanism of Adhesion Reduction

The aqueous chemistry of zirconium is complex and an important aspect is that polymerization occurs when solutions of zirconium salts are diluted.[8] The polymeric species formed can be cationic, anionic or neutral depending on the nature of the ligands. Structures of the polymeric species for ammonium zirconium carbonate (anionic) and zirconium acetate (neutral) are given in Figure 4.

Whilst it is accepted that zirconium salts form polymers in aqueous solutions,[15] there is little information about degree of polymerization. Jones[16] has recently reviewed the techniques which have been used in attempts to measure degrees of polymerization, and Clearfield[15] has commented that such studies are complicated by the sensitivity of the species to their environment and the slow attainment of equilibria. The base unit for these polymers contains



ANIONIC SPECIES FROM AMMONIUM ZIRCONIUM CARBONATE



NEUTRAL SPECIES FROM ZIRCONIUM ACETATE

FIGURE 4 Structures of zirconium polymers.

four Zr (IV) ions and under appropriate conditions the units may join together to produce larger molecules. Clearfield[15] has proposed that the base units contain four Zr (IV) ions arranged at the corners of a square, and that units may be joined at some or all of the corners by bridging hydroxide ions. The resulting polymers have 2-dimensional, sheet-like structures. Clearfield indicates that in suitable conditions species may be formed containing, 12–24 base units or 48–96 Zr(IV) ions. Squattrito, Rudolf and Clearfield[17] have determined the crystal structure of a polymer with 18 Zr ions.

We propose that the mechanism whereby zirconium compounds reduce adhesion is that they become attached to the surfaces of the adhesives. The mode of attachment can be by functional groups on the adhesive displacing ligands on the zirconium polymer. Surface carboxylic groups seem the most likely candidates for this and a possible mechanism is shown in Figure 5. Hydrogen-bonding is an alternative means of attachment, and the large number of hydroxide groups in the zirconium polymers favour this. Most of the adhesives studied contain ester groups on the polymer chains and under the conditions used some of these may hydrolyse. In the case of vinyl acetate units the product of hydrolysis would be vinyl alcohol units and with acrylates the product would be acrylic acid units. These

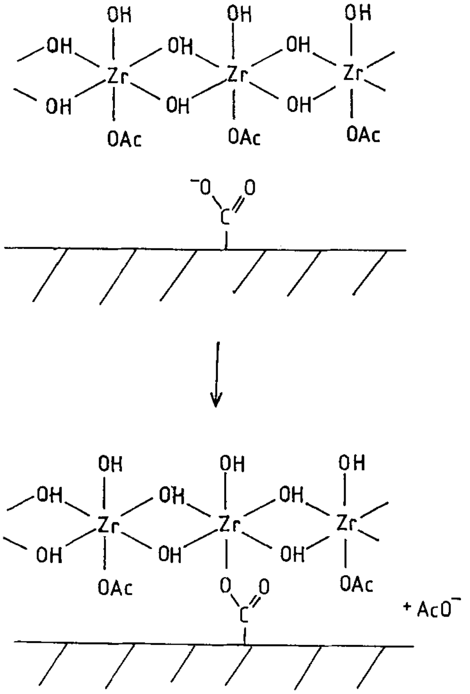


FIGURE 5 Reaction of zirconium acetate polymer with a surface carboxylic group.

could interact with the zirconium polymers by hydrogen-bonding and carboxylic group displacement respectively.

Once attached to the surface, the zirconium species could sterically hinder a larger part of the surface and thereby prevent or reduce adhesion. Thus even if the reactions which lead to attachment are inefficient, they may lead to much blocking of the surface, as only one attachment is needed to immobilize each zirconium macromolecule. Practical experience in the paper mill is that the zirconium salts are quickly consumed.

A problem that might be perceived with this argument is that the polymers of adhesives F and J do not contain ester, carboxylic or hydroxyl groups. However, at the 20 ppm level, reduction of adhesion by Bacote 20 and zirconium acetate is significantly less for adhesive F (Table IV) than for adhesives A, D and E (Tables I, II and III), and with Bacote 20 adhesion actually increases. Also esters are present in the rosin-based tackifiers in adhesive F and these may interact with the zirconium polymers by carboxylic interchange. In the case of Adhesive J, XPS showed that some oxygen-containing functional groups are present both before and after heating under the conditions used for preparing samples for adhesion measurements.

CONCLUSIONS

1) The acrylic, EVA and SBS adhesives studied were found to be impermeable to zirconium acetate solution although small quantities of zirconium were absorbed into the surface layers.

2) Zirconium compounds reduce the adhesion of all the adhesives under most circumstances. In some cases, adhesion reductions as high as 95% were observed for treatment with 20 ppm solutions.

3) Variables such as time and pH affect the adhesive–zirconium interactions. An increase in treatment time is beneficial for some adhesives and deleterious for others.

4) The contact test is only suitable for very tacky adhesives. The results from the contact test follow the same trend as those from adhesion measurements, i.e., large reductions in tack are observed after treatment with zirconium acetate solution.

5) The mechanism proposed is that zirconium polymers are attached to adhesive surfaces by carboxylic interchange or hydrogen bonding. The attached macromolecules block the surface.

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