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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Winkler-hechenleitner, Ana Adelina and Galembeck, Fernando(1990) 'Fractionation of Latex-Based Adhesives and Paints by Isopycnic Centrifugation', Separation Science and Technology, 25: 3, 293 — 308

To link to this Article: DOI: 10.1080/01496399008050333

URL: http://dx.doi.org/10.1080/01496399008050333

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SEPARATION SCIENCE AND TECHNOLOGY, 25(3), pp. 293-308, 1990

Fractionation of Latex-Based Adhesives and Paints by Isopycnic Centrifugation

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Abstract

Latex-based adhesives and paints can be fractionated by isopycnic sedimentation in density gradients, generated by osmocentrifugation. Fractions were obtained from a PVA-based adhesive, which differed in tacticity, as observed by ^{1}H NMR; calcium carbonate was easily identified in another product, after fractionation. In an acrylic-based latex paint the pigments contained PVA, although this polymer was not detected in other fractions. These results show that low-speed isopycnic sedimentation in density gradients is a convenient, gentle, inexpensive, and powerful method to fractionate complex particle admixtures. A marked advantage of this method is its ability to give fractions large enough for examination by other analytical techniques.

1. INTRODUCTION

Many adhesives and paints are based on latex particle dispersions, most often made of poly(vinyl acetate) (PVA) or acrylic copolymers. They may also contain various fillers and pigments, which are also of a particulate nature (*1, 2*).

Characterization of such dispersions requires the determination of their various components. This is a task for which laboratory methods are scarce. We have recently found that the technique of osmosedimentation

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(*3*) may be used to generate density gradients, which are helpful in particle separation by size and density (*4*).

In a further work, osmosedimentation was used to generate density gradients which were transferred to centrifugation tubes and then used in latex-based adhesive and paint fractionation. The results thus obtained are described in this work.

2. EXPERIMENTAL

2.1. Materials and Equipment

Percoll, a fine dispersion of polyvinyl pyrrolidone-stabilized silica, was obtained from Pharmacia (Sweden). Commercial, latex-based adhesives and paints were acquired from local distributors; they are not identified for ethical reasons. The osmocentrifugation cells were as described in previous works from this laboratory (*5*, *6*). They were fitted with membranes cast from cellulose acetate, as described in Ref. *7*, using a solution of 10 g cellulose acetate, 38 mL acetone, 35 mL acetic acid, and 21 mL H_2O.

Gradient formation and particle fractionation experiments were performed in a RC-3B Sorvall centrifuge fitted with a 6-L swinging bucket rotor. Density measurements were made via refractive index readings taken in a Bausch & Lomb Abbe refractometer.

2.2. Procedure for Density Gradient Generation

Percoll solution of the desired concentration is placed in one compartment of the osmosedimentation cell, water in the other. The cell is centrifuged for the given time and speed to generate a density gradient; this is transferred to a centrifugation glass tube by using a peristaltic pump. The sample to be analyzed is layered over the gradient and centrifuged again. After isopycnic equilibration of the tube contents (which is monitored visually), it is withdrawn (using a syringe or peristaltic pump, again) and divided in fractions which can be further analyzed by other (IR, NMR) methods after extraction and drying, as indicated in the Results section.

3. RESULTS

3.1. Heterogeneity in a PVA Latex. Isopycnic Fractionation

A Percoll density gradient was prepared by osmocentrifugation (initial density 1.123 g/cm^3, 10 min, 1000 rpm, 20°C) and transferred to a centrifugation tube. A 1-mL aliquot of a PVA latex was layered over this gradient and the tube was centrifuged again (20 h, 1500 rpm, 20°C), when the particle distribution depicted in Fig. 1 was obtained. The corresponding particle densities are also indicated in Fig. 1, and cover the range of 1.054 to 1.137 g/cm^3.

Fractions A-D in Fig. 1 were collected, dried, and extracted with toluene. ^{1}H-NMR spectra of these fractions are in Fig. 2. The following observations can be made of these spectra: (i) The peak at 2 ppm (assigned to acetate methyl groups) has three components: 2.02, isotactic (I); 2.00, heterotactic (H); 1.98, syndiotactic (S) (*8*). The intensity of the isotactic component increases with sample density. (ii) The unfractionated sample and Fraction D both display a triplet at 1.1 ppm and a quartet at 3.6 ppm, which do not appear in the fractionated, lower density samples. These signals are unequivocally assigned to CH_3CH_2O- groups (*9*) whose presence in this latex is unexpected. At this point we cannot state if it is due to some purportedly added constituent or if it is the result of accidental contamination.

3.2. Separation and Identification of Fillers and Pigments

3.2.1. From a PVA-Based Adhesive

A Percoll density gradient was generated by osmocentrifugation (initial density 1.133 g/cm^3; 10 min, 1000 rpm, 20°C) and transferred to a centrifugation tube. 1 mL of a PVA-latex based adhesive was layered on top of the gradient and centrifuged for 20 h, 1500 rpm, 20°C. The particle distribution thus obtained is observed in Fig. 3. The denser component (Fraction 13) was collected; an aliquot was used to obtain an IR spectum and another was extracted with toluene (4 × 5 mL, at room temperature). IR spectra of the extracted and unextracted samples are in Fig. 4 (A and

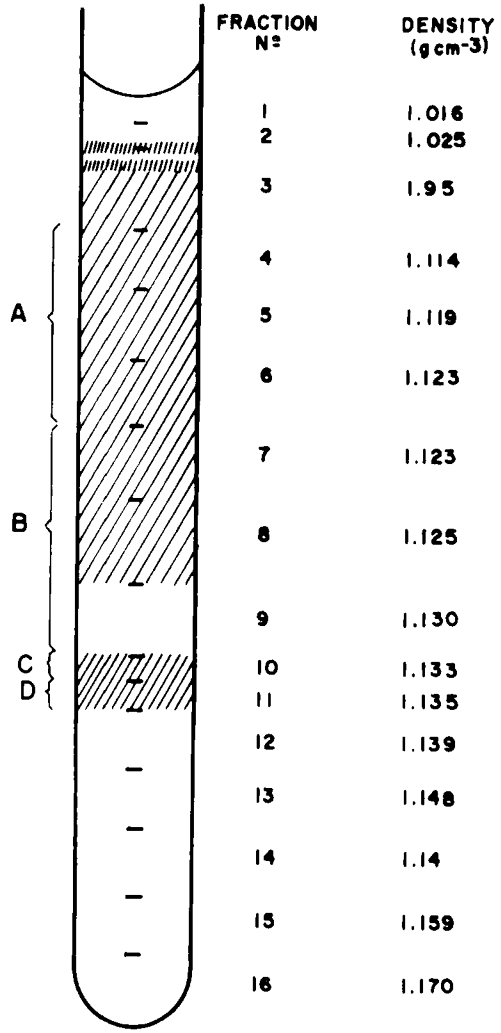
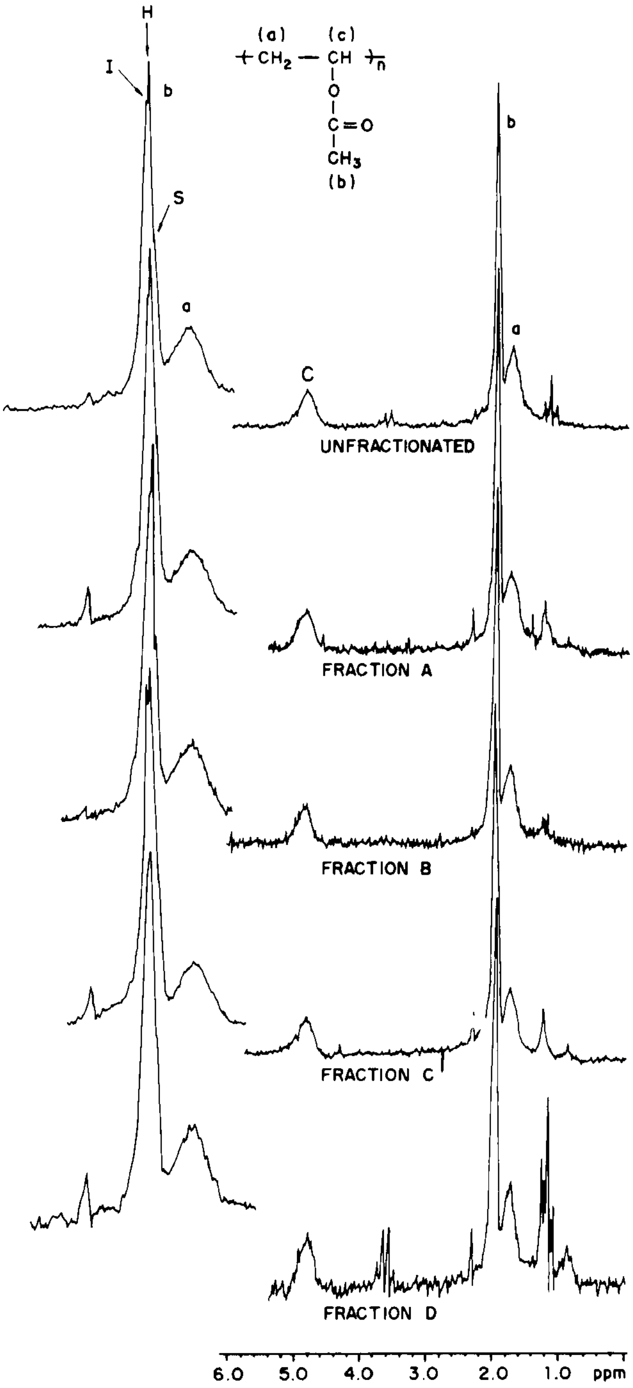


FIG. 1. Particle distribution of a PVA latex-based adhesive in a Percoll (initial density: 1.129 g/cm^3) density gradient. Experimental conditions: density gradient self-generated by osmocentrifugation: 10 min, 1000 rpm, 20°C; zonal centrifugation: 18 h, 1500 rpm, 20°C.

FIG. 2. ^{1}H-NMR spectra of a PVA latex-based adhesive and of fractions separated by centrifugation in a Percoll (initial density: 1.129 g/cm^3) density gradient. (I: isotactic; H: heterotactic; S: syndiotactic.) Solvent: CCl_4; reference: $CHCl_3$; instrument: Bruker AW-80. Concentration: unfractionated, 8%; Fractions A-C, 4.3%; Fraction D, 1.4% (fractions are identified in Fig. 1).


H
I
b
S
a
(a) (c)
-(CH2 — CH)n-
O
C=O
CH3
(b)
b
a
C
UNFRACTIONATED
FRACTION A
FRACTION B
FRACTION C
FRACTION D
6.0
5.0
4.0
3.0
2.0
1.0
ppm

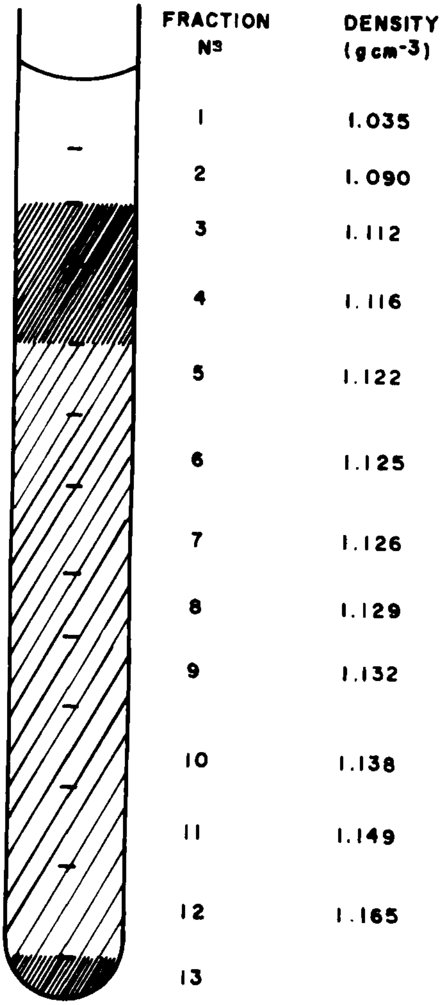


FIG. 3. Particle distribution of a PVA latex-based adhesive in a Percoll density gradient (initial density: 1.129 g/cm^3). Experimental conditions: density gradient self-generated by osmocentrifugation: 10 min, 1000 rpm, 20°C; zonal centrifugation: 18 h, 1500 rpm 20°C.

B). The solid was identified as calcium carbonate, containing some PVA, which resists extraction by toluene to some extent, and should thus be strongly adsorbed or occluded in the carbonate particles.

Toluene extracts of Fraction 13 and of Fractions 3 and 4 in Fig. 3 were evaporated, and spectra of the nonvolatile residues were taken (Fig. 5). This confirms that the only extractable calcium carbonate stabilizer is PVA.

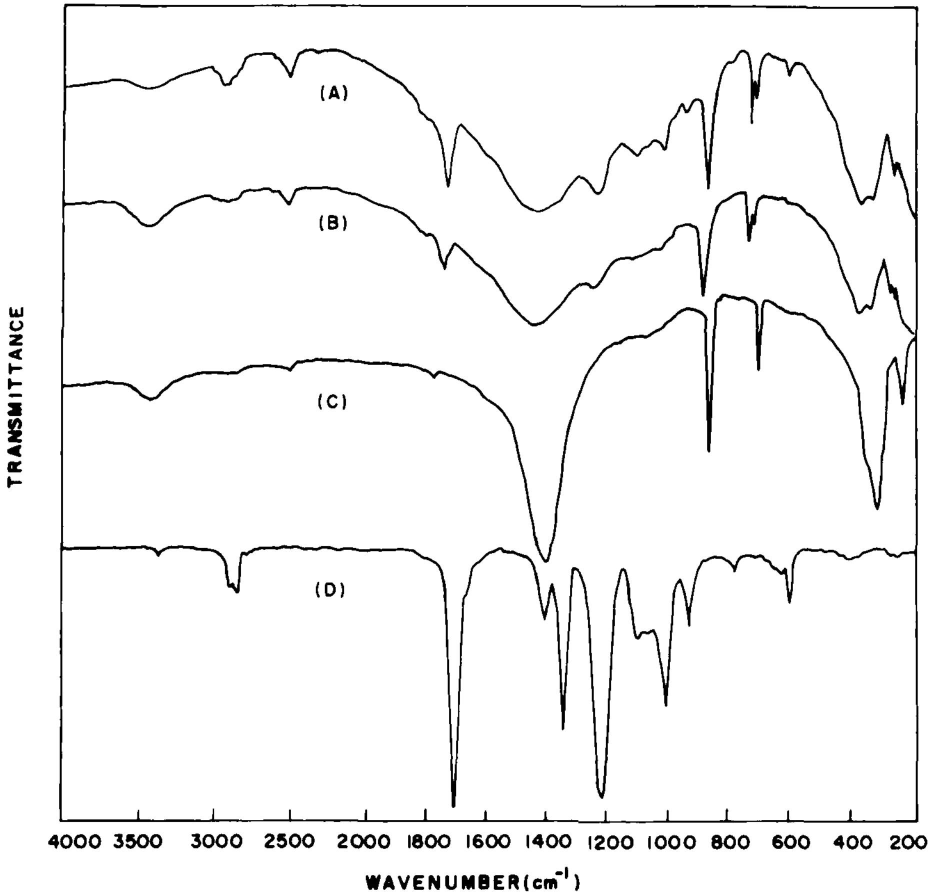


FIG. 4. Infrared spectra of (A) mineral fraction of a PVA latex-based adhesive, (B) Fraction A after 4 extractions with 5 mL toluene, (C) calcium carbonate (calcite), and (D) polyvinyl acetate from Ref. *18*.

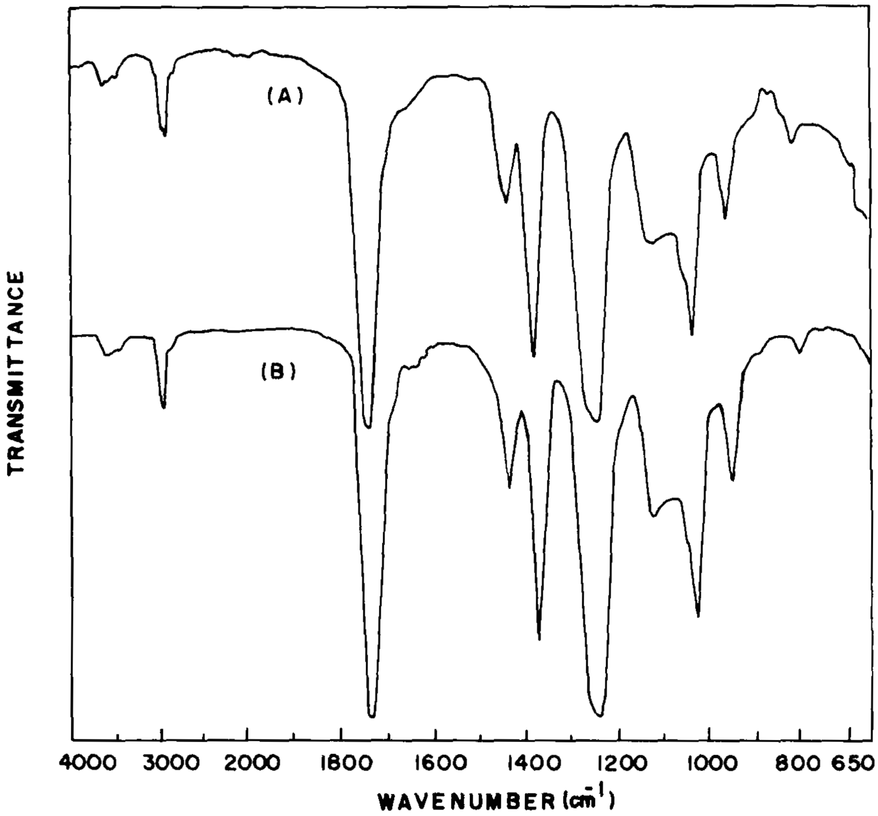
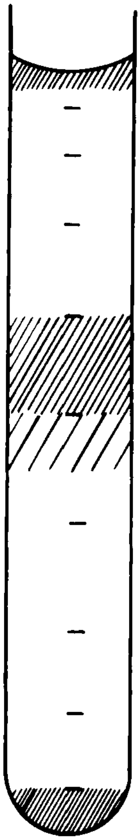


FIG. 5. Infrared spectra of the polymeric fraction collected from Fractions 3 and 4 (A) and in the toluene extract from Fraction 13 (B) (fractions are identified in Fig. 3).

3.2.2. From a PVA Latex-Based White Paint

A Percoll density gradient was generated (initial density 1.133 g/cm^3; 60 min, 2000 rpm, 20°C) by osmocentrifugation and transferred to a centrifugation tube. 0.5 mL of a white paint, PVA based, containing 22% solids was layered over the gradient and centrifuged for 26 h, 2000 rpm. Figure 6 gives the separation pattern obtained in this experiment. IR spectra of the material collected from Bands 5 and 10 show that these are, re-



FRACTION Nº	DENSITY (g cm^{-3})
1	0.987
2	1.008
3	1.040
4	1.067
5	1.099
6	1.135
7	1.171
8	1.199
9	1.231
10	

FIG. 6. Particle distribution of a PVA latex-based white paint in a Percoll density gradient (initial density: 1.129 g/cm^3). Experimental conditions: density gradient self-generated by osmocentrifugation: 60 min, 2000 rpm, 20°C; zonal centrifugation: 26 h, 2000 rpm, 20°C.

spectively, PVA and a mixture of titanium oxide and an aluminosilicate (Figs. 7 and 8).

3.2.3. From an Acrylic Latex-Based White Paint

A Percoll density gradient was generated by osmocentrifugation (initial density, 1.063 g/cm^3; 25 min, 2000 rpm, 20°C) and transferred to a cen-

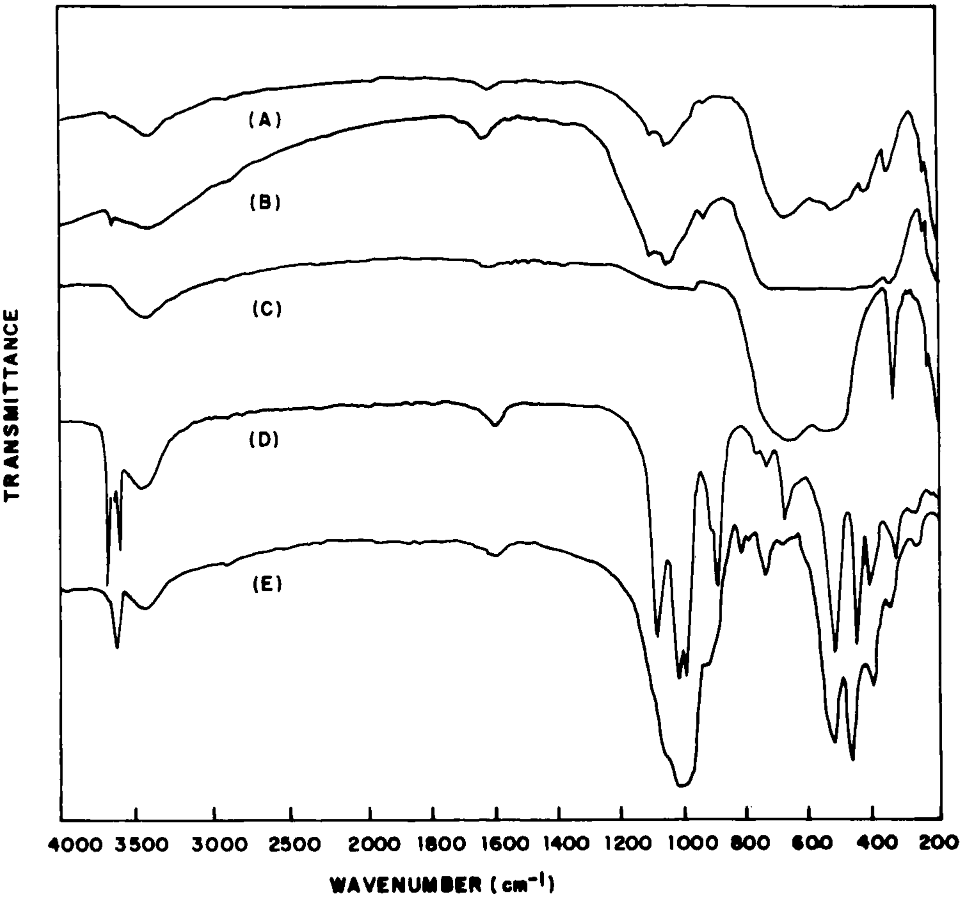


FIG. 7. Infrared spectra of the mineral fraction (from Fig. 6). (A) 0.5% KBr pellet. (B) 1% KBr pellet of a PVA latex-based white paint. (C) Titanium dioxide (1% KBr pellet). (D) Aluminum silicates (China clay) $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. (E) Potassium-aluminum silicate (mica) $K_2O\ 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ from Ref. *18*.

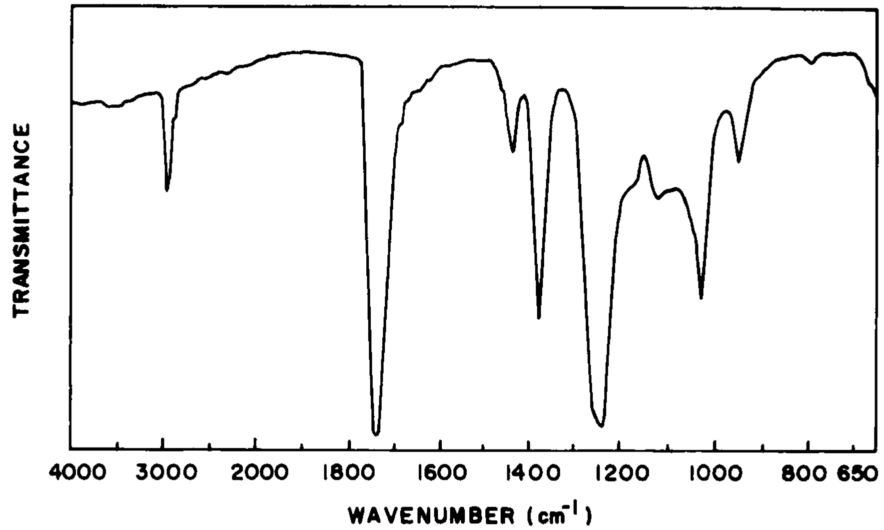


FIG. 8. Infrared spectrum of the polymeric fraction (collected from Fractions 5 and 6 of Fig. 6) of a PVA latex-based white paint.

trifugation tube. 1 mL of an acrylic-based white paint was layered over the gradient and centrifuged again for 20 h, 2500 rpm. The distribution of the particles thus obtained and the corresponding densities are shown in Fig. 9. Fractions 3, 4, and 5 of this gradient were collected, the polymer coagulated with a 5% w/v of $CaCl_2 \cdot 2H_2O$ in methanol solution and washed with distilled water, and finally dried. KBr pellets were prepared and IR spectra obtained (Fig. 10). This polymer is insoluble in common solvents of polystyrene and polyacrylates, thus preventing film casting from solution.

From these spectra we conclude that the base latex is a copolymer of styrene and one or both acrylic monomers: *n*-butylacrylate and 2-ethylhexylacrylate.

The absorbance ratio between the 1725 cm^{-1} (assigned to acrylate) and 695 cm^{-1} (assigned to styrene) peaks increases with particle density, as shown in Table 1, as expected. Another difference between the various fractions was in the absorbance at 470 cm^{-1}, which is higher in Fraction 3. This is assigned to metal carboxylates which could be formed either by hydrolysis of acrylate monomers or copolymer, or by polymer oxidation.

FIG. 9. Particle distribution of an acrylic latex-based white paint in a Percoll (initial density: 1.060 g/cm^3) density gradient. Experimental conditions: density gradient self-generated by osmocentrifugation: 25 min, 2000 rpm, 20°C; zonal centrifugation: 20 h, 2500 rpm, 20°C.

TABLE 1
Absorbances at 1725 cm^{-1} (acrylate) and 695 cm^{-1} (styrene) from the Spectra in Fig. 10

Fraction	$A_{1725} \pm 0.008$	$A_{695} \pm 0.008$	$\frac{A_{1725}}{A_{695}} \pm 0.05$
3	0.444	0.391	1.14
4	0.776	0.653	1.19
5	0.629	0.493	1.28

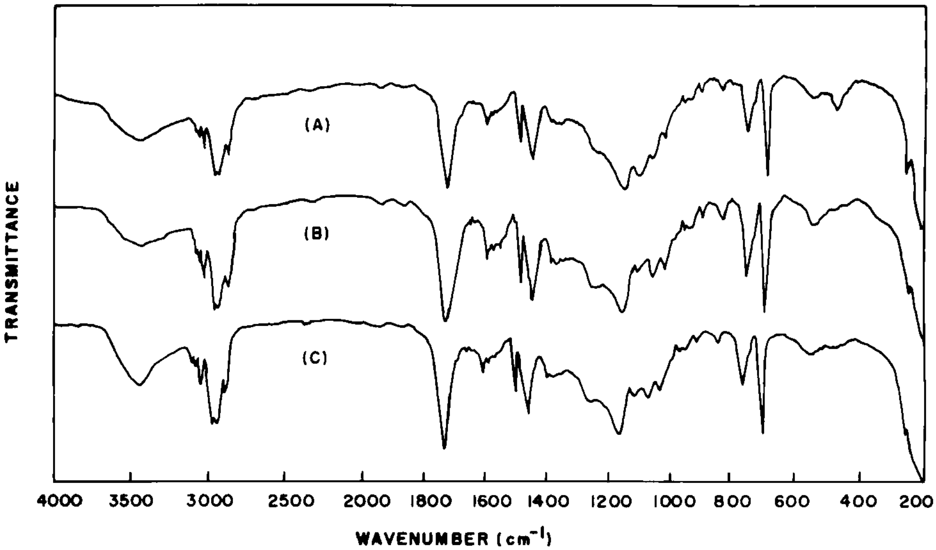


FIG. 10. Infrared spectra of the polymeric fraction of an acrylic latex-based white paint collected from the Fractions (identified in Fig. 9) 3: (A); 4: (B); 5: (C).

Infrared spectra of Fraction 10 in Fig. 9 reveals the presence of calcium carbonate, titanium oxide, and aluminosilicates (Fig. 11). PVA is also detected both in this residue (Fig. 11) and in its toluene extract (Fig. 12). The presence of TiO_2 and $CaCO_3$ was confirmed by x-ray diffraction in every case.

4. DISCUSSION

The fractionation techniques described in this work are powerful and easy to perform, although somewhat time-consuming. The cost of their implementation in any laboratory is low, since the equipment required is usually available.

The best demonstration of the effectiveness of these techniques is, perhaps, the detection of PVA bound to mineral fillers and pigments in an acrylic-based latex. The lack of cross-contamination, as demonstrated by the IR spectra, demonstrates the power of sedimentation techniques in difficult separations.

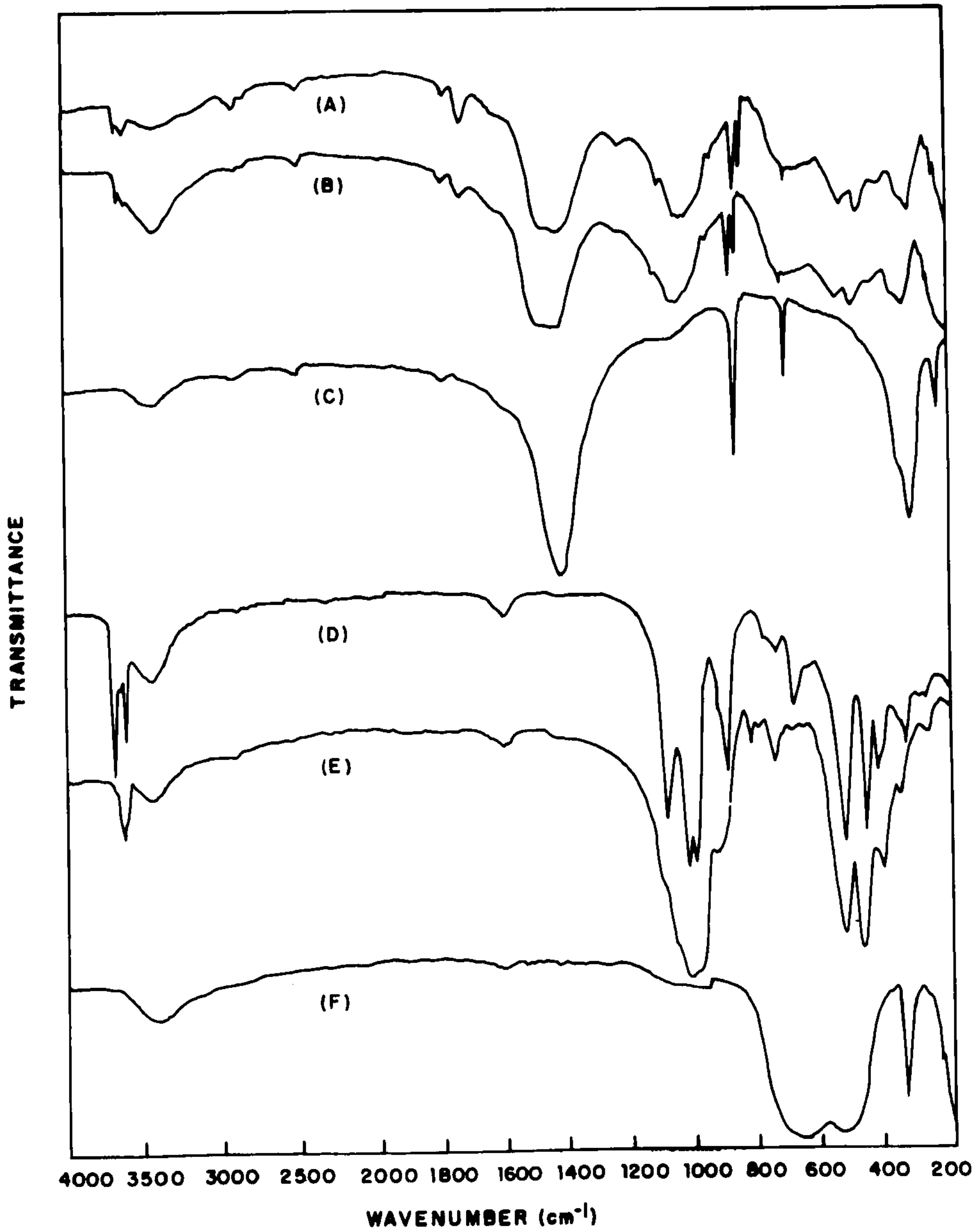


FIG. 11. Infrared spectra of the mineral fraction of an acrylic latex-based white paint collected from Fraction 10 (identified in Fig. 9): (A); of Fraction (A) after 4 extractions with 5 mL toluene (B); of calcium carbonate (calcite) (C); of aluminum silicates (China clay) (D); potassium aluminum silicate (mica) (E) (from Ref. *8*); and titanium dioxide (F).

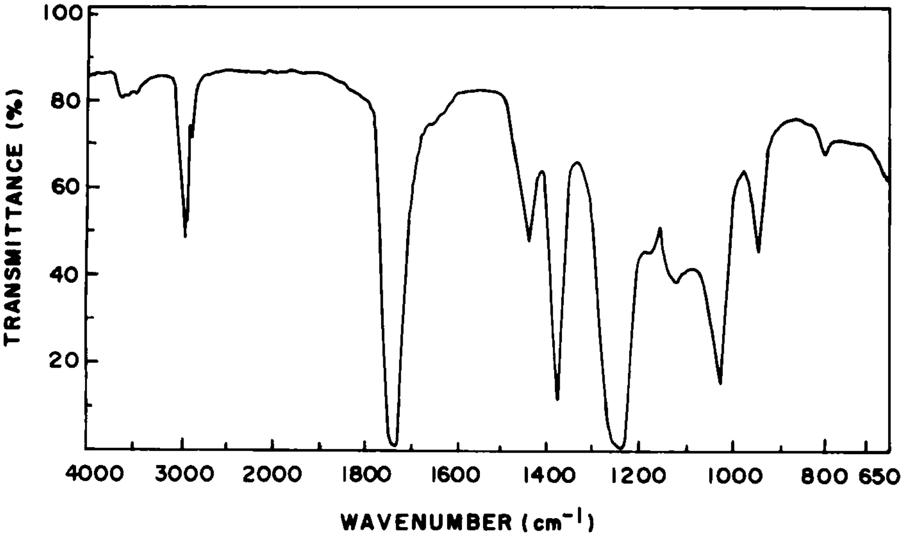


FIG. 12. Infrared spectrum of the polymer extracted with toluene from the mineral fraction (Fraction 10 in Fig. 9) of an acrylic latex-based white paint.

Samples used in this work were commercial products, and the information obtained is rather definite. These techniques should thus be useful with a variety of real samples.

Copolymers are particularly well suited to investigation by fractionation in density gradients (*10, 11*). In these cases, ultracentrifugation equilibrium experiments took 15 to 80 h; the interpretation of the experimental results is difficult when size- and composition-polydisperse samples are used. Lange (*12*) and Mächtle (*13*) established ultracentrifugation techniques by using density gradients suitable to separate and to characterize latex particles. Time requirements are small (10–30 min), but further particle analysis cannot be performed.

Considering the enormous success of sedimentation in density gradients in the fraction of biological particles (*14*), it is surprising that this technique has not been more widely used in the characterization of complex dispersions such as latex adhesives and paints. We think that the results described in this paper are examples of the immense potential of this technique.

Finally, we want to stress the preparative potential of this technique. It can be used to generate fractions suitable for examination by spectroscopic, diffraction, and other colloid-analytical techniques, such as various field-flow fractionation (*15–17*) methods.

Acknowledgments

A.A.W.H. was a Conselho Nacional do Desenvolvimento Cientifico e Tecnológico (CNPq) graduate fellow. F.G. acknowledges grants from Fundação de Amparo à Pesquisa do Estado de São Paulo and CNPq.

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Received by editor April 18, 1989