ence of the clay. This led to substitution of less reactive granular carriers, which gave biologically active granular formulations.

The application of CPMAS ^{13}C NMR to the study of labeled materials as granular formulations shows great promise for the characterization of such formulations. Our experience with 1 indicates that adsorption onto granules does not induce large chemical shift changes; the chemical shifts observed in the solution NMR spectra of 1 are similar to those seen in the solid state. The use of ^{13}C-labeled compounds involves no radioactivity, uses relatively cheap starting materials, and does not require large samples. (Each spectrum is obtained with about 20 mg of labeled active ingredient, and excellent signal to noise ratios can be obtained with overnight signal accumulation.) The state of the active ingredient on the granular carrier can be examined in a form typical for agricultural use, and delicate molecules need not be subjected to extraction or combustion analysis. In this work, qualitative information about the β-nitrostyrene/clay formulation was obtained from CPMAS ^{13}C NMR spectra. Because intensities in these spectra are easily and reliably quantitated, the technique should find wide application in more quantitative studies of granular formulations as well.

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Stirring Continuous Extraction of Aqueous Organic Compounds with Fluororesin as a Water/Organic Solvent Separator

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A stirring continuous-extraction apparatus equipped with a fluororesin in a water/extracting solvent separation chamber was designed to isolate solvent-extractable material from foods and beverages rapidly and to destruct the forming emulsion. The new apparatus was evaluated by experiments with dilute aqueous solution of several model mixtures of volatile compounds. A comparison study of the extraction efficiency has been made for the following three methods: stirring continuous, continuous, and batch extraction. The stirring continuous extraction has equivalent or better extraction efficiency than the other extraction methods for all the compounds tested. Most of the compounds showed nearly quantitative extraction after 2 h. This method has been successfully applied to the separation of flavors from wine.

Liquid–liquid extraction (batch or continuous) offers a very simple and efficient means of isolating flavors from foods (Wilson et al., 1985; Engel et al., 1988) and beverages (Shimizu and Watanabe, 1982). The batch method is very simple but labor-intensive. Vigorous shaking for a considerable time is required to make the method effec-

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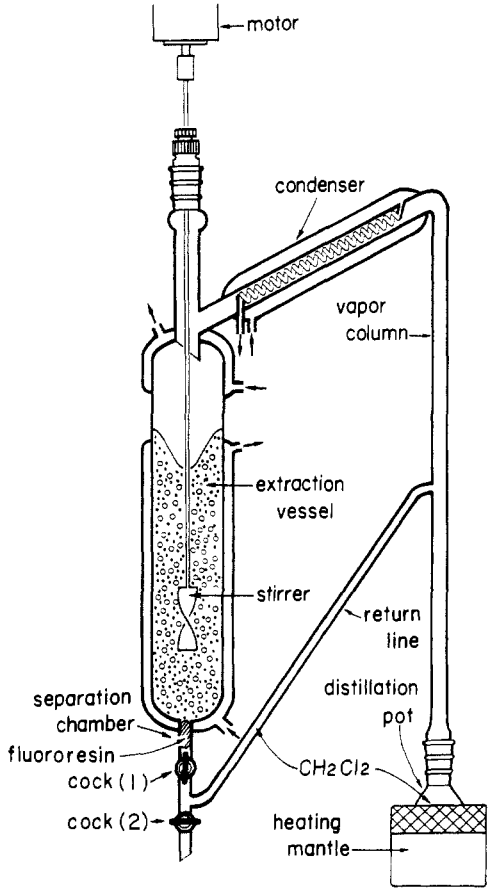


Figure 1. Stirring continuous-extraction apparatus.

tive. On the other hand, continuous extraction is too time-consuming to extract most solvent-extractable material from foods and beverages (Leahy and Reineccius, 1984).

Although extraction is a very powerful sample preparation method, this technique is limited to the analysis of foods containing no lipids unless a secondary isolation method (e.g., dialysis or distillation) is also applied. The formation of intractable emulsions in the presence of water-soluble proteins and/or carbohydrates may be encountered. In order to minimize artifact formation due to thermally induced change, vacuum distillation followed by solvent extraction is required on real food systems. If extraction must be the first step and if emulsions may be formed, then the emulsion formation should be avoided by use of very slowly moving parts and very slow countercurrent movement of the liquid. In order to improve efficiency by using a very large surface area, Stevens et al. (1969) designed a system consisting of a series of concentric perforated stainless steel tubes (designed for maximum surface area) rotated very slowly so that immiscible liquids are forced to move countercurrently. This work describes a new stirring continuous-extraction system equipped with a fluororesin in a water/organic solvent separation chamber to make the method effective and simple. Recovery of the pure compounds and the losses associated with this method were quantitatively investigated on experiments with model systems. This method has been applied to the separation of flavors from wine.

EXPERIMENTAL SECTION

Materials. All authentic chemicals were obtained from commercial sources. The white wine (Polaire) used was made in 1989 at Sapporo Wine Ltd. from Koshu grapes grown in the Yamanashi prefecture. Ultrapure water was obtained from an autostill all-glass Model WA-32 (Yamato Scientific Co., Ltd.).

Table I. Degree of Evaporation (%)[a] during Concentration from 80 to 1.0 mL by a Kuderna-Danish Concentrator and then 0.1 mL by N_2 Blow Down and Retention Indices of Compounds on an OV-101 Column (I^{OV-101})

compound	evaporation, % 0.25 ppm	evaporation, % 2.5 ppm	I^{OV-101}
	Model Mixture I		
alcohols			
propanol	82 ± 1	85 ± 1	543
butanol	49 ± 1	46 ± 2	645
pentanol	29 ± 1	23 ± 1	752
hexanol	22 ± 1	15 ± 2	855
heptanol	21 ± 2	13 ± 2	957
octanol	20 ± 2	13 ± 1	1056
nonanol	18 ± 3	14 ± 1	1161
lactones			
4-butanolide	23 ± 2	15 ± 1	885
4-hexanolide	19 ± 3	14 ± 1	1008
ketones			
2-octanone	22 ± 3	15 ± 2	959
2-decanone	22 ± 2	15 ± 1	1164
aldehydes			
hexanal	32 ± 2	28 ± 1	780
nonanal	22 ± 1	18 ± 2	1087
ester			
ethyl butyrate	25 ± 1	18 ± 2	784
	Model Mixture II		
acids			
acetic acid	66 ± 2	47 ± 2	600
butanoic acid	37 ± 1	27 ± 1	721
pentanoic acid	24 ± 1	19 ± 1	840
hexanoic acid	17 ± 1	12 ± 1	978
heptanoic acid	14 ± 3	12 ± 1	1059
octanoic acid	14 ± 1	11 ± 2	1156
phenols			
phenol	18 ± 1	16 ± 2	960
p-methylphenol	12 ± 1	11 ± 1	1056
p-propylphenol	10 ± 1	8 ± 2	1260

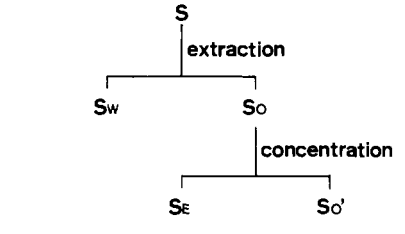
[a] Analyses by GC/MS. All recoveries based on an internal standard compound (isopentyl butyrate added after N_2 blow down).

Model Mixture of Volatile Compounds. Model mixtures of volatile compounds used in this study included propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, 4-butanolide, 4-hexanolide, 2-octanone, 2-decanone, hexanal, nonanal, ethyl butyrate, acetic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, phenol, *p*-methylphenol, and *p*-propylphenol (see Table I). A stock solution of all test compounds was initially made up in pure methanol. A 1-mL (or less) portion of this stock solution was diluted with ultrapure water to 1 L to obtain the desired concentration for analysis.

Gas Chromatography (GC). A Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector and a fused silica capillary column was used. Two types of wall-coated open tubular fused-silica capillary columns were used: 50 m × 0.22 mm (i.d.) coated with Carbowax 20M (CW 20M) and 50 m × 0.22 mm (i.d.) coated with OV-101. The columns were prepared in our laboratory (Shibamoto, 1982). The oven temperature was programmed from 80 to 200 °C and 2 °C/min. Nitrogen flow rate was 0.68 mL/min. The injector and detector temperatures were 250 °C. The injector split ratio was 1:100.

GC/MS Conditions. A Hitachi Model M-80B mass spectrometer was used under the following conditions: ionizing voltage, 70 eV; accelerating voltage, 3100 V; ion source temperature, 200 °C; carrier gas, helium. The gas chromatographic column and oven conditions were as described for the Hewlett-Packard gas chromatograph. Identification of all the peaks was made by comparison of their mass spectra and Kovats indices to those of authentic compounds. For some compounds, standard samples were not available to confirm positive identification. If the mass spectrum matched precisely that of published data and the retention could be estimated from the published data, the compound was listed as tentatively identified.

Scheme I



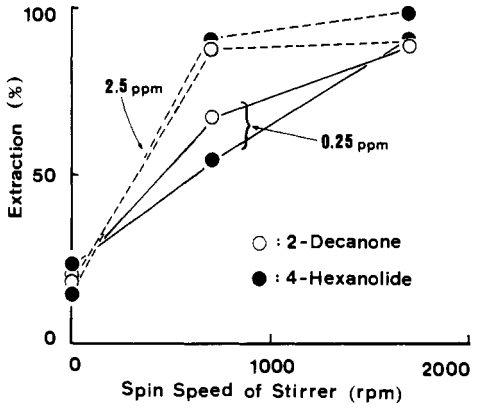


Figure 2. Relationships between revolutions per minute (rpm) of the stirrer for 0.5 h and the degree of extraction (%) from the model mixture at different concentrations of 2-decanone and 4-hexanolide.

Reversed-Phase High-Performance Liquid Chromatography (RP-HPLC). The HPLC system consisted of a Hitachi Model 635A equipped with a refractometer, Model RI-2 from Japan Analytical Industry Co. Ltd. Samples were injected with use of a Rheodyne syringe loading sample injector, Model 712D, with a 20-μL loop. The LC column used was purchased prepacked and was of the following type: a Capcell Pak C18 (Shiseido), 25 cm × 4.6 mm (i.d.), 5-μm particles. A precolumn (4 cm × 4 mm (i.d.)), which was dry-packed with the LiChrosorb RP-18 (Merck; 10-μm particles), was installed in front of the main column. The mobile phase was methanol–water (3:2, v/v), and the flow rate was kept at 1.0 mL/min. The model component was dissolved in the methanol–water (3:2, v/v) solution (0.5 %); a 20-μL sample was injected in the chromatograph. The retention times, t_R, were measured at 30 ± 0.1 °C. The column dead time, t_0, was determined by injection of potassium iodide solution. The capacity factors, k', were calculated as $(t_R - t_0)/t_0$.

Solvent Extraction. Solvent extraction was accomplished by stirring-continuous, continuous and batch extraction processes. An 80-mL portion of methylene chloride was used in each extraction method, and of it 30 mL was used for rinsing the glassware. The extract was dried over anhydrous sodium sulfate and then concentrated with a Kuderna–Danish evaporative concentrator to 1 mL in volume. Further concentration to 0.1 mL in volume was carried out with a dry nitrogen stream. Methylene chloride solution (0.1 mL) containing isopentyl butyrate and isopentyl hexanoate (750 or 7500 ppm) was added to the concentrated extract for quantitative GLC analysis. Injection volumes into the gas chromatograph were 2 and 3 μL for the 2.5 and 0.25 ppm model mixtures (see Table I), respectively. Three replicates were performed for each method of extraction.

Stirring Continuous Extraction. A diagram of the stirring continuous-extraction system is shown in Figure 1. The poly(tetrafluoroethylene) sheet (Polyflon Paper G-5d; Daikin Industries, Ltd.; 13 mm × 100 mm; thickness ca. 0.55 mm) was folded and placed in the separation chamber (4 cm × 6 mm (i.d.)). The distillation pot containing 30 mL of methylene chloride was joined to the vapor column. The Teflon cock (1) was opened, and the Teflon cock (2) was closed. The separation chamber was filled with methylene chloride (20 mL). The model mixture (2.5 and 0.25 ppm; 400 mL) or wine was placed in an extraction vessel, the temperature of which was kept constant at 20 ± 1 °C. The mixture solution or wine was vigorously stirred. Distillation from the flask was carried out for an arbitrary period of time. Zero time was taken to be when the condensed methylene chloride started dropping into the extraction vessel and the final time when heat to the methylene chloride was turned

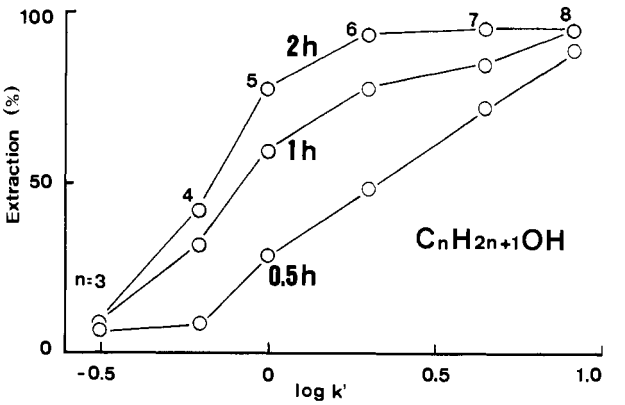


Figure 3. Relationships between the degree of extraction (%) of straight-chain alcohols with various times of stirring continuous extraction and their log k' (initial concentration of each compound in aqueous solutions, 0.25 ppm).

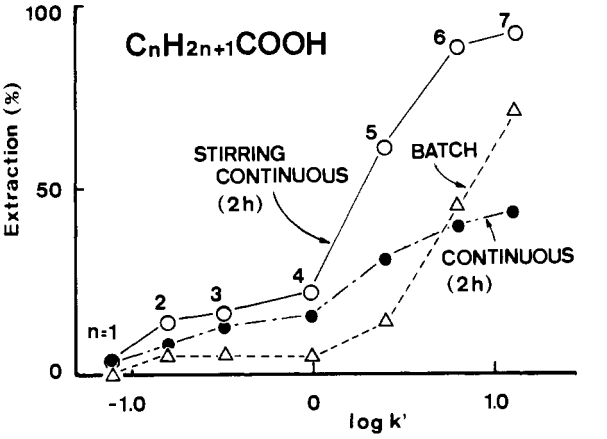


Figure 4. Relationships between the degree of extraction (%) of straight-chain acids and their log k' by using stirring continuous, continuous, and batch extraction methods (initial concentration of each compound in aqueous solutions, 0.25 ppm).

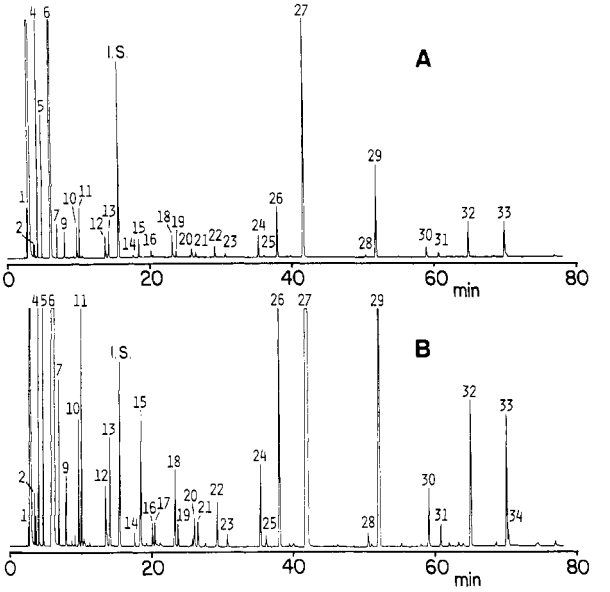


Figure 5. Chromatograms of volatiles extracted from wine by continuous (A) and stirring continuous extraction (B) for 0.5 h. A wall-coated open tubular fused-silica capillary column (50 m × 0.22 mm (i.d.)) coated with Carbowax 20M was used.

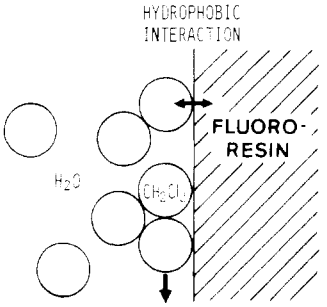


Figure 6. Model proposed for the destruction and separation of an emulsion composed of water and methylene chloride at the interface between fluororesin and water.

off. The methylene chloride was heated with a heating mantle such that a reflux rate of 120 drops/min was maintained.

Continuous Extraction. The same procedures with no stirring were followed for this extraction as described above for the stirring continuous extraction.

Batch Extraction. Four hundred milliliters of test solution (0.25 ppm) was placed in a separatory funnel. This mixture was then extracted three times with 17 mL of methylene chloride. Each extraction mixture was shaken 10 min by the shaking apparatus.

Estimation of the Degree of Recovery, Evaporation, and Extraction. A methylene chloride solution (5 g) containing the model mixture (0.02 and 0.002%, w/w) was added to 75 mL of methylene chloride. This diluted model mixture was concentrated in the same manner as that described in the solvent extraction section. A material balance for the model component during the extracting procedure is shown in Scheme I, where S is the initial weight of a component of the model mixture, S_w is the weight of the model component dissolved in water, S_0 is the weight of the model component extracted with methylene chloride, S_E is the weight of the model component evaporated during the concentrating procedure, and $S_{0'}$ is the weight of the model component recovered from the model mixture. The degree of recovery, evaporation, and extraction (%) can be represented by the following equations:

$$\text{recovery (\%)} = (S_{0'}/S) \times 100 \quad (1)$$

$$\text{evaporation (\%)} = (S_E/S) \times 100 \quad (2)$$

$$\text{extraction (\%)} = (S_0/S) \times 100 \quad (3)$$

Preparation and Analysis of Volatile Concentrates Extracted from Wine. A 400-mL sample of wine was extracted with 50 mL of methylene chloride on the stirring continuous-extraction apparatus for 0.5 h with and without stirring. The extract was dried over anhydrous sodium sulfate and then concentrated with a Kuderna–Danish evaporative concentrator to 1.0 mL in volume. Further concentration to 0.1 mL in volume was carried out with a nitrogen stream. Methylene chloride solution (0.1 mL) containing isopentyl hexanoate (4000 ppm) was added to the concentrated extract as an internal standard. Analysis of the concentrated extract was done by injecting a 2.0-μL sample into the gas chromatograph. The gas chromatographic column and oven conditions were those described for the Hewlett-Packard gas chromatograph.

Quantitative Assessment. Volatile compounds from wine prepared by extraction were analyzed. Quantitative data were then derived from GC/MS. Known amounts of all identified compounds were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the wine.

RESULTS AND DISCUSSION

The degree of evaporation (%) of each component during the concentration procedure and its retention index on the OV-101 column (I^{OV-101}) are shown in Table I. In general, the degree of evaporation (%) for a homologous series increases with decreasing I^{OV-101} value, which is closely related to its boiling point. The degree of evaporation at lower concentration (0.25 ppm) is usually higher than that at higher concentration (2.5 ppm). The relationships between the spin speed (rpm) of stirrer and the degree of extraction from the model mixture at different concentrations of 2-decanone and 4-hexanolide are shown in Figure 2. The degree of extraction increases with both increasing spin speed of stirrer and increasing concentration of the model component. The degree of extraction at 1700 rpm for 0.5 h is about 5 times higher than that with no stirring, but the other conditions are the same. Subsequent experiments of stirring continuous extraction were carried out at 1700 rpm. The degree of extraction of the substances during extraction depends on their partition constants (P). Reversed-phase high-performance liquid chromatography of chemicals has shown that the capacity factor (k') correlated well with the partition coefficient between octanol and water (P_{oct}) (Miyake and Terada, 1978; Noel and Vangheluwe, 1987). Figure 3 demonstrates the extraction of straight-chain alcohols with various times of the stirring contin-

Table II. Volatile Components Identified in the Extract from Koshu Wine Using the Stirring Continuous-Extraction Apparatus for 0.5 h with and without Stirring (1700 and 0 rpm, Respectively)

peak no.[a]	compound	mg/kg of wine[b] A[c]	mg/kg of wine[b] B[d]	Kovats index on CW 20M I_u(A)[e]	Kovats index on CW 20M I_u(B)	Kovats index on CW 20M I_k[f]
1	ethyl acetate	0.08	2.55	839	839	843
2	isobutyl acetate	0.08	0.64	992	988	992
3	ethyl butyrate	0.04	0.16	1014	1014	1016
4	isobutyl alcohol	2.74	8.09	1044	1041	1043
5	isoamyl acetate	0.73	1.61	1103	1103	1105
6	isoamyl alcohol	13.92	49.34	1169	1169	1165
7	ethyl hexanoate	0.18	0.68	1212	1212	1212
8	acetoin	0.29	0.68	1242	1241	1242
9	hexyl acetate	0.04	0.25	1246	1245	1250
10	ethyl lactate	0.38	1.35	1298	1298	1298
11	hexanol	0.40	1.87	1309	1309	1314
12	acetic acid	1.18	3.19	1386	1383	1387
13	ethyl octanoate	0.24	0.87	1411	1410	1414
14	ethyl 3-hydroxybutyrate	0.04	0.22	1465	1464	1469
15	2,3-butylene glycol (levo)	0.23	1.89	1475	1474	1476
16	isobutyric acid	0.13	0.33	1505	1503	1508
17	2,3-butylene glycol (meso)	g	0.42	1507	1507	1512
18	4-butanolide	0.33	1.15	1560	1559	1559
19	butyric acid	0.12	0.46	1560	1559	1563
20	isopentanoic acid	0.08	0.42	1602	1600	1605
21	ethyl decanoate	0.07	0.24	1610	1609	1605
22	3-(methylthio)-propanol	0.18	0.61	1648	1646	1645
23	unknown			1667	1666	
24	unknown			1734	1733	
25	2-phenylethyl acetate	0.03	0.14	1757	1755	1760
26	hexanoic acid	0.96	2.89	1771	1769	1769
27	2-phenylethyl alcohol	2.82	8.11	1832	1834	1835
28	diethyl malate	0.07	0.42	1959	1957	1957
29	octanoic acid	1.40	3.72	1977	1977	1980
30	2-methoxy-4-vinylphenol	0.14	0.59	2096	2094	2094
31	unknown			2123	2122	
32	decanoic acid	0.40	1.46	2183	2181	2185
33	monoethyl succinate	0.77	2.16	2261	2260	2264
34	4-vinylphenol	g	0.17	2275	2274	2274

[a] Refers to peaks numbered in Figure 5. [b] Calculated from the extraction (%) value of each compound. [c] Continuous extraction. [d] Stirring continuous extraction. [e] Kovats index of unknown. [f] Kovats index of authentic sample. [g] The value of milligrams per kilogram of wine less than 0.01.

uous extraction as a function of log k'. The relatively low degree of extraction for propanol was due to the only slightly favorable liquid–liquid partition coefficient. Octanol showed better than 90% extraction in 0.5 h. The degree of extraction for several of the alcohols, including butanol, pentanol, hexanol, and heptanol, was improved as a function of extraction time. The stirring continuous extraction for 1 h was found to yield a degree of extraction for model components comparable to that with batch extraction.

A comparison of stirring continuous, continuous, and batch extraction for isolating straight-chain acids is presented in Figure 4. Under the conditions used in this study, the continuous extraction was more effective than the batch extraction for isolating CH_3COOH–C_5H_{11}-COOH. On the other hand, our data indicate that there was less $C_6H_{13}COOH$ and $C_7H_{15}COOH$ for continuous extraction compared to batch extraction. It is obvious that stirring continuous extraction was substantially more effective than both continuous and batch extraction. The values for the degree of extraction by stirring continuous extraction tend to be equal to the sum of their values for both continuous and batch extraction. Although extraction is very powerful sample preparation method, interference by the formation of intractable emulsions in the presence of water-soluble proteins and/or carbohydrates may be encountered. For example, the stirring of wine produces an emulsion. However, extraction by the stirring continuous extractor with use of a fluororesin for the purpose of the separation of water and methylene chloride was possible. The chromatograms of volatiles extracted from wine by continuous extraction and stirring continuous extraction are shown in Figure 5. The identified components and concentrations of each compound are listed in Table II. The stirring continuous extraction was a more effective extraction method than continuous extraction. For processes involving the absorption of a liquid into a solid surface, the concept of a critical surface tension of the solid, γ_c, appears to be of considerable value in characterizing the solid surface. Liquids of surface tension equal to or less than γ_c will spread spontaneously over the surface. The fluororesins and polyethylene, etc., are chemically resistant and their γ_c values [poly(tetrafluoroethylene), 18.5 dyn/cm; poly(vinylidene fluoride), 25.0; poly(chlorotrifluoroethylene), 31.0; polyethylene, 31.0) (Zisman, 1964)] are near or not more than γ_L values (surface tension of liquids) of methylene chloride (27.8 (20 °C)) and far less than that of water (72.9 (20 °C)) (Jasper, 1972). The destruction and separation of an emulsion into its components (water and methylene chloride) can be proposed as shown in Figure 6. Methylene chloride probably exists at the surface of a fluororesin by hydrophobic interaction between them. On the other hand, water is probably far from the surface of the fluororesin. The individual particles of water and methylene chloride were then separated on the basis of the difference in their specific gravity.

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