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detailed

ACETYL TRIBUTYL CITRATE
SOLUBILITY FROM POLYVINYL FILM

The solubility of acetyl tributyl citrate from a polyvinyl chloride film plasticized with acetyl tributyl citrate was determined for aqueous systems at various pH's and for a 5% salt solution at a neutral and an acid pH. The solubility of acetyl tributyl citrate in lard oil, peanut oil, mineral oil, and soybean oil was also determined.

By virtue of its composition, and its chemical and physical properties, acetyl tributyl citrate and its related compounds would seem to be desirable plasticizers for films used in contact with foods.

As information on the solubility of the plasticizer from the film in various solvents such as water at various pH values, and from common edible oils, is important ~~and required by the Food and Drug Administration and Meat Inspection Division (USDA) for sanction of this type use,~~ the following data has been obtained:

1. Aqueous Systems

The five following group tests were conducted in order to evaluate the possible loss of acetyl tributyl citrate in aqueous systems:

1.	Water	adjusted to - pH	3.0
2.	Water	" " - pH	7.0
3.	Water	" " - pH	10.0
4.	5% Sodium Chloride Solution	" " - pH	3.0
5.	5% Sodium Chloride Solution	" " - pH	7.0

In all cases the solutions were buffered to the desired pH by the use of hydrochloric acid or sodium hydroxide.

A strip of the film (0.003 inches thick) 6 inches wide and approximately 52 inches long (315 square inches) was threaded through a series of rolls under uniform tension of 1/2 inch diameter glass rod which served as the bottom spool and separated the film, allowing uninterrupted contact between the film and solvent. The entire film was exposed to the solvent as the upper spools were also under the solvent at all times.

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All strips weighed 13.5 grams and had an area of approximately 315 square inches. All strips of film were from the same production batch and were 0.003 inches thick.

The films were suspended in a square type battery jar and kept completely covered with 8 liters of the solvent used for extraction. The tanks were held in a constant temperature room of 23° C. for a period of 3-1/2 months.

At the end of the test period, the film was removed from the tanks, washed free of any salts, measured, dried to constant weight at 40° C. (4 hours) and the weights recorded. A control batch of film was dried under the same conditions and the loss in weight was negligible. The loss in weight of the entire film is recorded in Table I together with other pertinent data from these tests.

Extraction

The solvent solutions, after a vacuum filtration through filter paper to remove any dust which might have entered the jar, were thoroughly extracted with carbon tetrachloride in order to concentrate the plasticizer dissolved by the solvent. A total of 1,150 cc of carbon tetrachloride was used for the extraction of each 8 liters of solvent. The solvent was extracted three times in 750 cc batches. Each 750 cc batch was extracted three times with 35 cc portions of carbon tetrachloride. The wet carbon tetrachloride extraction was dried by shaking with an excess of anhydrous sodium sulfate, filtered, and concentrated under vacuum. Each residue was taken to dryness, weighed, and redissolved in a small amount of carbon tetrachloride and finally made to the volume of 10 cc. This 10 cc solution was used for the infra-red absorption assay for the quantitative amount of acetyl tributyl citrate extracted.

In order to establish that it was practical to use this method of extraction, a preliminary test was made in which a known quantity of acetyl tributyl citrate was added to a large volume of water, subjected to the extraction procedure, and concentrated under vacuum. The residue was weighed and assayed chemically for acetyl tributyl citrate. The results indicated that this method of extraction was suitable, as the results were accurate within 2%.

As it was desired to have a very specific means of measuring acetyl tributyl citrate extracted, the use of infra-red absorption techniques were investigated. Since the infra-red absorption maximum of the ester carbonyl group is very specific and sensitive, this was chosen for possible assay use. Using a known concentration of acetyl tributyl citrate and carbon tetrachloride, the infra-red absorption curve of the ester was recorded using a Perkin-Elmer Model 12B infra-red spectrometer equipped with sodium chloride optics, using a fixed cell of approximately 0.100 mm. thickness. This was repeated using a series of known concentrations of acetyl tributyl citrate solutions in carbon tetrachloride. The maximum absorption of the ester carbonyl group was found at 1747 cm^{-1} (5.72 microns) using the height of this maximum (after correction for absorption due to carbon tetrachloride

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and water vapor) as a measure of the acetyl tributyl citrate concentration. It was established experimentally that concentrations between 1.0% and 0.1% could be determined with an accuracy of ± 5% of the total amount present, assuming no other ester was present. Obviously, results obtained by this method are a maximum, in that they would include any other esters present, and any decomposition products of acetyl tributyl citrate which might be formed containing a carbonyl group.

In order to check the efficiency of extraction, and prove the acceptability of this method of analysis, control runs were made where known amounts of acetyl tributyl citrate were added, put through the entire extraction procedure, and assayed by infra-red analysis. Results of these tests show that reproducible assays can be obtained with a maximum variation of ± 4%, which falls within the limits of the precision of the instrument.

The film was formulated to contain 24 parts of acetyl tributyl citrate in 126 parts of the finished product, or 19.04% acetyl tributyl citrate. (The bulk of the film of the resin from Geon 11X Latex.)

The pertinent data obtained from these tests are summarized in Table I.

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TABLE I

LOSS OF ACETYL TRIBUTYL CITRATE FROM POLYVINYL CHLORIDE FILM - AQUEOUS SOLVENTS

Sample	No. 1	No. 2	No. 3	No. 4	No. 5
Solvent	Water	Water	Water	5%NaCl	5%NaCl
pH	3.0	7.0	10.0	3.0	7.0
Weight of Extracted Material (CCl_4 Solubles) (Mg.)	19	25	33	10	18
Weight of Extracted ATBC* (Infra-red Analysis) (Mg.)	20	26	13	12	19
Percent ATBC Extracted (Based on 19.04% of original film weight)	0.78%	1.01%	0.51%	0.47%	0.74%
Weight of ATBC Extracted Per Square Foot of Surface (Mg. Per Sq. Ft.) (One Side)	9.2	11.9	6.0	4.6	8.7
(Two Sides)	4.6	5.9	3.0	2.3	4.4
Total Loss in Weight of Film Through Solvent (Mg.)	161	130	134	102	214

* ATBC - Acetyl Tributyl Citrate

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These data show that only a small amount of acetyl tributyl citrate is extracted by water in either acid neutral or alkaline pH or by a 5% salt solution at either an acid or neutral pH. Although 2,565 milligrams of plasticizer was present in each test strip, only from 12 to 26 milligrams of acetyl tributyl citrate were extracted in these tests. The solubility at a neutral pH was higher than acid both for the water and salt solutions, however, the solubility seemed to decrease at pH values higher than neutral. The salt solutions seemed to extract a smaller amount of ester than does the water.

The weight of ester extracted per square foot of surface has been expressed both for calculation using one side of the film for exposed surface area and also using two sides. Obviously, the quantity extracted per square foot when expressed for one surface is ~~a more conservative figure for the Food and Drug Administration's use~~. Undoubtedly, if sufficient time were allowed, one side of the film should be capable of giving the complete extraction as encountered in this test.

The quantity of carbon tetrachloride solubles parallels quite closely the amount of acetyl tributyl citrate extracted with the exception of batch No. 3, the alkaline water solution, where a considerable excess of carbon tetrachloride solubles were obtained over the acetyl tributyl citrate extracted. The last line in Table I shows that on a basis of loss of weight of the film, a considerable amount of other materials were extracted from the films in these tests.

The wet appearance of the films in tests 1, 2, and 3, were very foggy, whereas the 5% sodium chloride solutions 4 and 5, gave only a slight foggyness to the wet film. All films, however, were clear after drying. They all showed exceptionally good flexibility after extraction and subsequent drying. In these tests a large excess of solvent was employed, for 8,000 grams of solvent being used for 13.5 grams of plasticized film, or 2.565 grams of plasticizer.

2. Oil and Fat Systems ~~FAT SOLUBILITY~~

As films plasticized with acetyl tributyl citrate might be used in contact with fatty foods, these tests were conducted in order to determine the amount of solubility of acetyl tributyl citrate from films using this ester as a plasticizer. As acetyl tributyl citrate is completely miscible with peanut oil, lard oil, and soybean oil meal, and is miscible in mineral oil to approximately 29% by volume, it was considered desirable to determine the extent of oil solubility of the ester from the film.

Attempts were made to develop a specific assay for the presence of acetyl tributyl citrate in the solvent oil, however, they were not successful in that reproducible quantities could not be obtained. Use of changes of refractive index, infra-red absorption, etc. proved to be of no value in this case. M. C. Reed has reported a method for

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measuring fat solubility of plasticizers (Ind. Eng. Chem. 35, 896, 1943) which measures the loss of weight of the film when suspended in the oil.

This procedure was followed with slight modifications. A 5" X 5" square of the film (0.003 inches thick) was loosely rolled and suspended in a graduate containing 100 cc of the test oil. The film was removed at regular intervals, completely washed of the adhering oil by rinsing in five successive baths of petroleum ether, and brought to constant weight by drying in an air oven at 60° C. (one-half hour) . A control test strip washed and dried in the same manner showed a negligible loss in weight.

The following Table II summarizes the results obtained by this method. The values for percent loss in plasticizer have been calculated on the basis that any change in weight of the film has been a result of loss of plasticizer by solubility in the oil. This method naturally makes the assumption that there is no pick-up of the oil by the film.

Values are given for solubility after one month and eight months testing. Several tests were taken in the first month, however, they seem to show an almost linear relationship of loss of plasticizer with time during this period. The rate of solution of the plasticizer seems to drop off with time after one month, as a linear relationship no longer exists, although the plasticizer continues to dissolve in the oil with extended time.

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TABLE II

LOSS OF ACETYL TRIBUTYL CITRATE FROM POLYVINYL CHLORIDE FILM - OIL SOLVENTS

Sample	No. 6	No. 7	No. 8	No. 9
Solvent (Oil)	Lard	Mineral	Peanut	Soybean
% Loss (Basis ATBC)				
One Month	1.5%	1.3%	2.7%	1.8%
Eight Months	8.6%	7.6%	9.7%	8.5%
Loss (Basis ATBC) (Mg. Per Square Foot Surface)				
Calc. One Side				
One Month	17	15	31	21
Eight Months	100	68	112	98
Calc. Two Sides				
One Month	8.5	7.5	15.5	10.5
Eight Months	50.0	34.0	56.0	49.0

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The strips in oil were held in a room at 23° C. A large quantity of oil was used with reference to the amount of film, approximately 90 grams of oil being employed for 1.0 grams of film or 0.19 grams of plasticizer in the film.

The solubility in all oils seems to follow the same general pattern, mineral oil having the lowest solubility, peanut oil having the highest solubility.

The loss of acetyl tributyl citrate, as milligrams per square foot of surface, has been expressed on a basis of one surface exposed, and two surfaces exposed. Obviously, in these tests two surfaces were exposed, however, this difference is largely academic for it is just a matter of time until the solvent would undoubtedly be able to extract throughout the entire thickness of the film which is 0.003 inches.

The data on fat solubility is naturally based upon the assumption that any change in weight of the film after soaking in the oil results from the extraction of the plasticizer from the film. If any component of the film other than the plasticizer were to dissolve in the oil the values reported for oil solubility of the plasticizer from the film would be high, and if the oil had any solubility in the film the results reported would be low.

These limitations are unfortunately inherent to this method of analysis, which does not employ a specific assay for the ester extracted. We have, however, not been able to develop any quantitative method for the measurement of the ester in oil, as we have been able to do in aqueous systems.

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