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PHOTOGRAPHIC FILM CLEANING SOLUTIONS

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1 Claim. (Cl. 252—171)

The present invention relates to photographic film cleaning solutions comprising methyl chloroform (1,1,1-trichloroethane) and particularly to the stabilization of such solutions to provide inhibition of the natural tendency of methyl chloroform to attack metallic aluminum.

Methyl chloroform has proved to be a very useful cleaning solvent for photographic film due to its good solvent properties with respect to oils and greases, non-flammability, low toxicity and other favorable characteristics. It has no detrimental effect on cellulose ester base when properly used in accepted cleaning procedures. As is well known, however, methyl chloroform often attacks aluminum metal. This notorious reaction is not merely a corrosion effect but actually is evidenced by evolution of a gas (hydrogen chloride) and production of a purple to black color and a precipitate. If exposure of the aluminum to the solvent is continued after the reaction is underway, the reaction will become quite vigorous. However, the reaction is erratic. It occurs sometimes when not expected and at other times it fails when it is expected to occur. In any event, it is sufficiently troublesome to render uninhibited methyl chloroform generally unsuitable for film cleaning use since in such use contact of the film cleaning solvent with aluminum metal often may occur. Reaction of methyl chloroform with metal is not limited entirely to aluminum but has been observed with some alloys of zinc. However, inhibition of the normal activity of methyl chloroform toward aluminum appears in every instance to result also in inhibition of the activity with respect to the zinc alloys.

For use as a solvent in fields other than photographic film cleaning, it has been found possible to stabilize methyl chloroform sufficiently to prevent reaction with aluminum. However, it has also been found that many of the stabilizers are not tolerated by photographic film and all of them, as far as I am aware, may produce detrimental effects if extreme care is not used. Among the detrimental effects which these stabilizers or inhibitors exhibit on photographic film, the two most significant perhaps are solvent activity for the film and tendency to deposit a noticeable residue or smear which remains on the film for an unusually long time.

It is an object of the present invention to provide new inhibitors for methyl chloroform and new film cleaning compositions containing the same, which inhibitors will eliminate reactions between the methyl chloroform and aluminum and at the same time provide compositions having utility for film cleaning without the bad effects on film which result from the use of the known and otherwise satisfactory inhibitors.

I have discovered that compounds selected from the group consisting of dihydropyran, 2-methyl furan and 1,3,3-trimethoxypropene, when added in a small amount to methyl chloroform, inhibit reaction of the methyl chloroform with aluminum and provide a solvent having no adverse effects on photographic film when used in customary film cleaning methods. In accordance with

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my invention a stabilizing amount (generally in the range of about 1 to 5%, preferably $3 \pm 1\%$, by weight of the methyl chloroform) of the inhibitor is added to a solution of methyl chloroform, and the solution is used for film cleaning after thorough mixing, preferably after standing for at least about 24 hours.

The method of preparing the inhibited solutions involves nothing more than the mere mixing together of the two constituents and may therefore be accomplished by any means known to the art as long as sufficient agitation and/or time is utilized to provide a homogeneous mixture, or rather solution.

It is felt that as a practical matter the less inhibitor added to the methyl chloroform the better, as long as effective inhibition is obtained. While the amount of the inhibitor to be employed in accordance with the present invention is not deemed to be critical, it is a general rule that the concentration of the inhibitor is of some significance in its effectiveness. Thus, from the tables which appear below it will be noted that a compound which is a good inhibitor at the three percent or five percent level may be ineffective at the one percent level. Three percent appears to be a good average value for the inhibitors of the invention. At the same time there is no reason to believe that these inhibitors will not give operative solutions when used in concentrations of more than five percent by weight, although in the tables below no value greater than five percent is shown (and in practice none should be necessary). The invention therefore contemplates the use of any concentration of the disclosed compounds which is operative in the respect that it is sufficient to inhibit reaction of the methyl chloroform with aluminum. Thus an "effective amount" will include inhibitor concentrations as low as operative and as high as and higher than five percent as long as the resulting composition is useful and operative as a photographic film cleaning solution.

The inhibited solutions may be used in any of the well-known and accepted film cleaning procedures customarily used with prior solvents such as those comprising carbon tetrachloride, or 1,1,2-trichloro-1,2,2-trifluoroethane and/or n-heptane. Preferably film is cleaned by gently but firmly wiping its surface with a pad of a soft, lint-free fabric such as velvet, the pad having been moistened with the inhibited solution. Mechanical devices such as are normally employed in the cleaning of long continuous lengths of motion picture film may be used to advantage. These devices normally comprise a pair of opposed pads providing a path for the film therebetween, the pads being spring-pressed toward each other to engage the film with the proper pressure on both of its faces, the pads being continuously fed from a reservoir with a regulated amount of cleaning solvent.

The invention is illustrated in the following examples.

EXAMPLE 1.—INHIBITING ABILITY

Samples of commercial grade methyl chloroform were prepared for testing with the new inhibitors. Each of the inhibitors dihydropyran, 2-methylfuran, and 1,3,3-trimethoxypropene was added to different samples of the methyl chloroform in varying amounts representing one or more of the concentrations one, three, and five percent by weight of the methyl chloroform. Pieces of 16-gauge type 2S aluminum metal were immersed in the samples of the freshly prepared solutions and all were allowed to stand in a stoppered test tube until a reaction was observed or until a definite time had passed without occurrence of a reaction. These tests were repeated using redistilled methyl chloroform. The data in Table I represent either the shortest time in which a reaction was first observed or the longest time that an inhibitor was under observation with still no reaction having taken place.

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Table I

Compound Added	Inhibitor Concentration by Weight					
	Commercial Solvent			Redistilled Solvent		
	1%	3%	5%	1%	3%	5%
dihydropyran.....		3M	-----	h	5M	-----
2-methylfuran.....		3M	-----	3.5M	3.5M	-----
1,3,3-trimethoxypropene..	3M	-----	-----	4.5M	4.5M	3.5M

h=reacted within one hour after mixing.
M=no reaction for one month, at which time test was ended.
nM=no reaction within n months, when testing was ended.

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EXAMPLE 3.—EFFECT OF INHIBITED SOLUTIONS ON CELLULOSE ESTER PHOTOGRAPHIC FILM BASE

Samples of methyl chloroform containing suitable concentrations of each of the three inhibitors of the invention were prepared. These samples were evaluated as to the effect thereof on various types of cellulose ester film and cellulose ester plastic film cores. Results are shown in the following table.

Table IV

Compound	Percent Added by Weight	Appearance Ratings, Residue from—		Percent Added by Weight	Attack Rating			
		Wiping	Droplet		AP	AB	A3	PAB
2-methylfuran.....	3	No.....	Yes.....	3	No.....	Curl..	No.....	S&S
dihydropyran.....	5	No.....	Yes.....	3	No.....	—	No.....	SS&S
1,3,3-tri-methoxypropene.....	5	No.....	Yes.....	3	No.....	—	No.....	SS&S

AP=cellulose acetate-propionate film base.
AB=cellulose acetate-butyrate film base.
A3=high acetyl, i. e. cellulose tri-acetate film base.
PAB=cellulose acetate-butyrate plastic film core.
S&S=swelling and softening.
SS&S=slight swelling and softening.
—=not tested.

EXAMPLE 2.—REPRODUCIBILITY OF INHIBITING EFFECT

Portions of the inhibitors dihydropyran, 2-methylfuran, and 1,3,3-trimethoxypropene were each added to a different sample of uninhibited practical grade methyl chloroform in an amount of three percent by weight of the latter, thoroughly mixed therewith, and the resulting solutions allowed to stand for one day. Each of the solutions was then divided into twelve parts and into each part was placed a ½ inch by 2 inch piece of roughened 16-gauge aluminum (Type 2S). The thirty-six samples were stoppered and allowed to stand while they were observed periodically for evidence of reaction over a thirty-day period. The results of these tests are shown in Table II. Another series of tests was made on a new batch of samples which were observed for a seven day period with results as shown in Table III.

Table II

Compound	Concentration by Weight	Number of Tests	Number of Reactions
dihydropyran.....	Percent 3	12	0
2-methylfuran.....	3	12	0
1,3,3-trimethoxypropene.....	3	12	0
methyl chloroform (pract.).....	100	12	12

Table III

Compound	Concentration by Weight	Number of Tests	Number of Reactions
dihydropyran.....	Percent 1	12	0
Do.....	2	12	0
Do.....	3	12	0
2-methylfuran.....	1	12	0
Do.....	2	12	0
Do.....	3	12	0

EXAMPLE 4.—ABILITY OF THE INHIBITORS TO MAINTAIN THEIR INHIBITING EFFECT AFTER SHELF-AGING FOR A PERIOD OF MONTHS

Three solutions of methyl chloroform containing three percent by weight respectively of dihydropyran, 2-methylfuran and 1,3,3-trimethoxypropene were prepared and placed in stoppered glass vessels which were held in storage for six months. A few days after termination of the six month period these solutions were removed from storage and into each was placed a strip of aluminum sheeting. The samples then were kept under observation with the aluminum partially immersed for six days, at the end of which time all samples still were free of any evidence of reaction between the methyl chloroform and the aluminum.

EXAMPLE 5.—USE OF INHIBITED SOLUTION FOR CLEANING FILM

A velvet pad was dampened with a solution of methyl chloroform containing 3% dihydropyran as prepared in Example 1, and a length of cine film was passed in contact with the damp pad. The film leaving the pad was wound onto an aluminum reel and placed in storage overnight. When the film was subsequently unwound no tendency of the convolutions to adhere to each other was noticed. No deposits or smears could be detected on the film by visual inspection. There was no noticeable damage to the surfaces of the reel or of aluminum vessels or other aluminum components of the equipment used in the cleaning operation. No change in the photographic quality of the film was observed but it was exceptionally clean, substantially all dust, grease, and finger smears having been removed.

I claim:

A method of cleaning photographic film comprising wiping the surface of the film with a cleaning member moistened with methylchloroform containing from 1% to 5% by weight of dihydropyran, whereby grease and dirt are removed from the film without damage to the

film base or to the photographic emulsion layer, and reaction between the methylchloroform and any aluminum parts with which it comes in contact is inhibited.

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