PREPARATION OF SOME NEW FIRE-RESISTANT SAMPLES AND THEIR APPLICATION

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SUMMARY: Samples of polyurethane- halogenated fatty acids were prepared by impregnating and treating some strips of paper (waste) with typical solution. It was composed of a fatty acids (coconut oil, and Castor oil), a polyalcohol (glycerol)-dissolved in toluene and butyl acetate 1:1-toluene diisocyanate and variable proportions of halogenated fatty acids (trichloroacetic acid and/or bromoacetic acid), in presence of dibutyltin dilaurate which acts as a catalyst and stabilizer. The prepared polyurethane- halogenated fatty acids samples were screened as fire-resistant paper. Standard test method was used to evaluate these samples. Some of it (optimum equivalent ratio, isocyanate/carboxyl was 2.28 based on carboxyl group in bromo acetic acid) were found to be efficient as fire-resistant paper.

Key words: Fire-resistance, halogenated fatty acids, polyurethane.

INTRODUCTION

Flame-retardant treatment of paper, and paper board (3) is of importance in packaging, decoration, electrical application, structural and utility uses (1,7).

Flammability can be reduced by several techniques (17); a) reduced fuel available by using a thermally stable resin or an inert filler, b) Produce a thermal barrier by charring or using glass formers, c) Quench the chain reactions in the flame by adding free radical scavengers.

A large number of flame-retardant coating formulations containing various phosphours (4, 5,18) bromine, hydrated alumina and chlorine compounds, were found to be the most effective for net and ant.

Halogens, particularly bromine compounds, occupy an important position today among the fire-extinguishing and flame-retardant agents. Bromine generally is more effective than chlorine (6,12). Halogens attached to aliphatic carbon are more effective than those attached to aromatic groups (9) the position of bromine atoms in the polymer also influences flame retardance (8,13,15).

The amount and type of halogen present determines the extent of improvement of flame retardance of polyurethanes (14).

The formulation of urethanes must take into consideration every possible reactive constituent in all of the intermediates (10,11). Carboxylic acid react readily with isocyanates, the reaction rate being dependent on the acid strength. The reaction proceeds via an unstable intermediate whose decomposition depend on the type of isocyanate and carboxylic acid (2, 16).

Diisocyanate+hydroxyl=urethane (RNHCOOR)
Diisocyanate+carboxyl=amide (NHCO)
RNCO+R COOH=RNHCOR
Ar NCO+R COOH=Ar NHCO NH Ar+R-C-O-C-R)

MATERIALS AND METHODS

Materials

Castor oil: Having the following specifications:
Specific gravity 0.966 hydroxyl number 165
Acid number 1.9 equivalent weight 340
Coconut oil: Having the following specifications:

Physical properties	Chemical properties (%)
Specific gravity 0.917-0.919	Lauric acid 45.4
Melting point, °C24 - 27	Myristic acid 18
Equivalent weight 220	Palmitic acid 10.5
Saponification value 250-264	

Isocyanate: Toluene diisocyanate (TDI) mainly a mixture of 80% 2,4 and 20% 2,6 Toluene diisocyanate.

Methods

Preparation of fire-resistant samples: Through the present work, several formulations were tried and the best samples were

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obtained by mixing the components in the proportions, show in Table 1. The general procedure for formulation was as follows:

A typical solution which have been employed in the impregnation to obtain fire-resistant paper were prepared by dissolving castor oil, coconut oil, and a glycerol in a mixture of organic solvents containing equal weights of toluene and butyl acetate, followed by addition of trichloroacetic acid and/or bromo acetic acid in different proportions with agitation at room temperature.

The whole solutions were mixed with dibutyltindilaurate which acts as a catalyst and heat stabilizer. The previous solutions were added to toluene diisocyanate with agitation for 30 minutes at 60°C. Next, twelve strips of waste of paper were impregnated and treated with the above mentioned solutions. After impregnation, the samples were dried at room temperature during 72 hours to form the required samples p_1, p_2 ...., p_{12} respectively Table 1.

The required samples were tested as fire-resistant paper according to the standard methods [ASTM D 1433-58 (1966) and DIN 53382] (Tables 1, 2).

RESULTS AND DISCUSSION

In the present work, a fatty acids (coconut oil and castor oil), a polyalcohol (glycerol), toluene diisocyanate, and a hologenated fatty acids (Trichloroacetic acid and/or bromoacetic acid) were reacted together to form polyurethane-halogenated fatty acids samples.

The results in Tables 1, 2 show that the burned length, and burning time sec., of the sample P_9 (composed of bromoacetic acid 35 gm, isocyanate/carboxyl 2.28) is 4 mm, and 27 sec. (Non-Burning), of the sample P_8 (composed of bromoacetic acid 25 gm, NCO/CHOOH 3.18) is 6 mm, and 30 sec. (NB), of the sample P_7 (composed of bromoacetic acid 15 gm, NCO/COOH 5.27) is 12 mm, and 60 sec. (NB), and of the sample P_6 (composed of bromoacetic acid 5 gm, NCO/COOH 15.8) is 55 mm, and 156 sec. (B). This means that the fire-resistance of these four samples is in the order $P_9 > P_8 > P_7$. Since P_9 has the lowest value of burned length and burring time. This indicates that the best fire-resistance property improves gradually with increasing the amount of bromoacetic acid from (Nill to 35 gm) or with decreasing the optimum equivalent used ratio from (15.8 to 2.28).

Again the burned length, and burning time of the sample P_5 (composed of trichloroacetic acid 35 gm, NCO/COOH 2.7) is 25 mm and 70 sec. (NB) of the sample P_4 (composed of trichloroacetic acid 25 gm, NCO/COOH 3.8) is 36 mm, and 79 sec. (SE), of the sample P_3 (composed of trichloroacetic acid 15 gm, NCO/COOH 6.3) is 50 mm, and 150 sec. (B), of the sample P_2 (composed of trichloroacetic acid 5 gm) NCO/COOH 19) is 50 mm, and 160 sec. (B) and of the sample P_1 (absence of halogenated compounds) is 74 mm, and 220 sec. (B) This means that the fire-resistance of these five samples is in the order $P_5 > P_4$ since P_5 has the lowest value of burned length and burning time.

This indicates that, the best fire-resistance property improves gradually with increasing the amount of trichloroacetic acid from (Nill to 35 gm) or with decreasing the NCO/COOH from (19 to 2.7).

It is clear that, the impregnating paper with polyurethane trichloroacetic acid (Chlorine 64.9%) or/and polyurethane-bromoacetic acid (Bromine 57.5%) improves its resistance to fire and reduces its burning time and after glow, due to the fact that, the halogenated compounds depends on the production of HX (X=halogen) -a non-combustible gas as well as flame propagation inhibitor. HX is known to inhibit flame propagation by a free radical mechanism (7).

On the other hand, the burned length and burning time of the sample P_{12} (composed of 17.5 gm trichloroacetic acid and 17.5 gm bromoacetic acid) is 10 mm, and 45 sec. (NB), of the sample P_{11} (composed of 12 gm trichloroacetic

Table 1: Formulations of the components used in preparing fire-resistant paper.

Samples / Components		P	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}
Concount oil		Non-treated	35	35	35	35	35	35	35	35	35	35	35	35
Castor oil			55	55	55	55	55	55	55	55	55	55	55	55
Glycerol			10	10	10	10	10	10	10	10	10	10	10	10
Dibutyltindilaurate			0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tricchloroacetic acid			-	5	15	25	35	-	-	-	-	23	12	17.5
Bromoacetic acid			-	-	-	-	-	5	15	25	35	12	23	17.5
TDI			50	50	50	50	50	50	50	50	50	50	50	50
Toluene:butylactetate			50:50	50:50	50:50	50:50	50:50	50:50	50:50	50:50	50:50	50:50	50:50	50:50
Equivalent used ratio	NCO/COOH*		-	19	6.3	3.8	2.7	-	-	-	-	4.07	8.14	5.3
	NCO/COOH**		-	-	-	-	-	15.8	5.27	3.18	2.28	6.6	3.45	4.5
NCO/COOH and -OH (total)			5.08	4.87	4.45	4.1	3.77	4.87	4.45	4.1	3.77	3.77	3.77	3.77

* Trichloroacetic acid Equivalent used ratio=eq. used NCO/eq. used COOH Weight (gm)=Eq. used X eq. weight

** Bromoacetic

Table 2: Fire-resistant test on prepared (strips of paper) samples.

Samples / Test	P	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}
Burning time, sec	53	220	160	150	79	70	156	60	30	27	50	42	45
Burning lenght, mm	82.5	74	50	50	36	25	55	12	6	4	18	9	10
Rating	B	B	B	B	SE	NB	B	NB	NB	NB	NB	NB	NB

N=burning NB=non-burning SE=self-extinguishing

acid and 23 gm bromoacetic acid) is 9 mm, and 42 sec. (NB), and of the sample P_{10} (composed of 23 gm trichloroacetic acid, and 12 gm bromoacetic acid) is 18 mm, and 50 sec, This means that the fire-resistance of these three samples is in order $P_{11} > P_{12} > P_{10}$. Since P_{11} has the lowest value of burned length and burning time.

This shows that the fire-resistance property improves gradually by increasing the amount of bromoacetic acid that trichloroacetic acid (23 gm; 12 gm) in the formulations of the polyurethane halogenated acids samples respectively. This due to the fact that, the fire-resistance activity of bromine-containing compound was found to be greatly enhanced than that of their analoges of chlorine-containing compound is generally greater than that of their bromine analoges (7).

From the experimental data, it can be concluded that:

1. The prepared samples can be arranged according to the best of fire-resistance property (lowest burned length mm, and burning time sec., -non-burning NB) as follows:

$P_9 > P_8 > P_{11} > P_{12} > P_7 > P_{10} > P_5 > P_4$

2. The rate of burned length, and burning time indicates the flammability or rapidity of burning.

3. The prepared fire-resistance polyurethane- halogenated fatty acids samples improve gradually with a) increasing the amount of halogenated fatty acids bromoacetic acid and/or trichloroacetic acid from (Nill to 35 g), b) decreasing the optimum equivalent used ratio of isocyanate/carboxyl from (15.8 to 2.28 in case of bromoacetic acid) and (19 to 2.70 in case of trichloroacetic acid).

4. The sample P_9 proved advantageous to the other samples due to, increase of amount of bromoacetic acid (35 g) and the optimum equivalent used ratio was (2.28).

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