Influence of Flame Retardant on Leather Fat Liquoring and Fire Resistance

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Abstract: Common nitrogen—phosphorus flame retardants (KZR-2, SC-968, FR-102) in textile were imposed on the fat section of leather. Then the flame retardants were put into leather with the amount of 0%, 0.5%, 1.0%, 1.5%, 2.0%, 3%, 6%, 9%, 12% and 15% of various fat liquoring agents (synthetic oil, fish oil, vegetable oil and lecithin) to change the rate of absorption, and non-flame property changes of leather were also made. Dosage of fat liquoring changes in the rate of absorption was measured by oven and dichloromethane, and fire resistance was measured by limited oxygen index, vertical combustion, and smoke density. The results showed that flame retardants (KZR-2, SC-968 and FR-102) made fat liquor absorption rate of leather increase by more than 40%, with the increased order of the KZR-2, SC-968, and FR-102. KZR-2 improved leather absorption of fat liquor rate in the order of synthetic oil, fish oil, lecithin, vegetable oil. When the amount of KZR-2 got to 1.5%, influence of fat-liquoring on leather fire resistance of was best. As a result, leather can reach at the level of retardant.

Key words: flame retardant; leather; fat liquoring agent; fire resistant

1 Introduction

Fat liquoring is an important section of leather production. After fat liquoring, the right amount of grease is absorbed by leather products, all fibers being surrounded by oil which increases fiber mobility each other, so that the leather has become soft, folding. And its tensile strength, elongation, water resistance has been markedly improved. In addition, fatliquor also plays a minor complement tanning, which makes leather tough. But during the process of leather fat liquoring, fatliquor often can not be totally absorbed, which not only causes a great deal of waste oils but also increases the amount of suspended solids in water, in order to increase COD, BOD values, resulting in nutrient of water [1]. According to statistics, in recent years, arising from the annual leather 80 million ton ~ 120 million ton of industrial waste water contains about 1 thousand ton ~ 0.5 thousand ton of fatliquor. These fatliquors increases costs of water treatment. So how to improve the absorption rate of the leather processing fatliquor has become an immediate problem to solve a large number of leather workers.

The study of Q.J. Wang et al [2] found that common vegetable oil, animal oil, synthetic oil, phospholipids were migrated from internal leather to the leather surface due to heat during of combustion process. These oils played a roll of combustion accelerant agent which made leather continue burn. The author studied the factors of flame-retardant on leather, it was found that some flame retardants that were

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imposed on fat liquoring of the leather section, not only cooperated with fatliquor and improved the utilization of fatliquor .At the same time, flame retardants can also enter the internal leather and combinate with proteins to improve the flame resistance of leather, the order of collaboration with fatliquor and flame retardant was continued to be intensively studied in order to enhance the absorption of fatliquor rate and improve the fire retardant leather for provide a theoretical basis for industrialization.

2 Experimental

2.1 Reagent and Equipment

Formic acid, chemical pure, Tianjin Chemical Reagents First Factory; sodium formate, analytical pure, Tianjin Chemical Reagents First Factory; sodium carbonate, analytical pure, Tianjin Rui Jinte Chemicals Ltd.; degreasing agent, Clariant Company; synthetic fat-liquoring agent, Shanghai Leather Chemical; Organic phosphorus retanning agent FCC, industrial, Clariant Company; synthetic fat-liquoring agent SE, Shanghai Leather Chemical ;phosphated oil NLM, industrial; Clariant Company; fish oil NC, industrial, Clariant Company; sulfated castor oil, industrial, Shanghai Leather Chemical; flame retardant KZR-2, industrial, xi'an kelida Chemical LTD; flame retardant SC-968, industrial, Shuang Er Jie Beijing high-tech Co., Ltd; flame retardant FR-102, industrial, Qingdao United Chemical Co., Ltd. Glycerin, AR, Jinan Fine Chemicals Corporation; dichloromethane, AR, Tianjin Chemical Reagents First Factory; GI Heat Cycle Stainless Steel Electrical Testing Chassis, Wuxi City Derun Light Machinery Factory; HWS-150 constant temperature and constant wet case, Shanghai Shanlian Laboratory Equipment Ltd; ZF-3-level vertical combustion detector, Nanjing Shangyuan Apparatus Limited; HC-2C oxygen index detector, Nanjing Shangyuan apparatus Limited ; YM-3-type materials smoke density machine, Nanjing Shangyuan apparatus Limited ; Electronic Balance, Austrian House of International Trade (Shanghai) Co., Ltd; HH-S digital thermostat oil bath pot, Jintan Medical Instrument Factory.

2.2 Experimental Screening Process of Fatliquor and Flame Retardants

Wet blue pig skin was chosen as Raw materials for the selected experimental, Cr_2O_3 content of 3.87%, moisture 66.7%, the thickness of 0.8mm. Wet-blue leather along the back line on both sides of the corresponding sample was selected from a rectangular, vertical direction with back line was regarded as length; parallel with back line was regarded as width for the sample, length and width of each sample size of 30cm × 15cm. Ensuring the amount of other reagents and process parameters under the same conditions, dose 17% of synthetic fat-liquoring agent SE, fish oil NC, Sulfated castor oil and phosphated oil NLM were respectively chosen as fatliquor, 0%、0.5%、1.0%、1.5%、2.0%、3%、6%、9%、12%、15%KZR flame retardant were pick out in order to filter fatliquor which was anti-leather incombustibility minimal impact and type and amount of flame retardant which can improve the absorption rate of fatliquor;

Drum rotation speed 30r/min

Degreasing water 200%, 40℃;
degreasing agent 0.5%,
formic acid 0.2% 60min, checking pH 3.5, draining;

Water washing water 200%, two each from 10min

Retanning water 200%, 40℃;
Sodium 1.0%, 30min
sodium carbonate 0.5% 3×10+30min pH 5.0
FCC 6% 120min
sodium carbonate 0.7% 2×10min pH 5.5 draining

Water washing water 200%, two each from 10min

Counteracting water 100%, 35℃;

sodium carbonate 0.2%, 20min pH6.0 draining

Water washing water 200%, two each from 10min

Fat-liquoring water 100%, 40 ℃

fat-liquoring agent (SE, NC, ME, NLM) 17%, 40min

flame retardant （KZR、SC-968、FR-102） X% 30min

water 50℃, 100% 60min

formic acid 1.5%, 40min (three times each interval at 10min) pH 3.0~3.2;

Water washing: two each from 10min draining;

2.3 Detection Method of Flame-Retardant

Making use of oxygen index, vertical burn and smoke density can measure anti-incombustibility of leather.

2.3.1 Oxygen Index

Oxygen index is a means of 52mm × 50mm specimen, in a mixture of oxygen and nitrogen gas to keep sample burn 3 minutes which is required for the concentration of oxygen percentage[3].

$OI = [O_2]/([N_2] + [O2]) \times 100\ \%$

$[O_2]$ In particular to maintain the combustion temperature of the minimum oxygen flow, mm^3/s;

$[N_2]$ Nitrogen flow for the corresponding, mm^3/s

The greater the oxygen index is, the oxygen required to maintain combustion higher, that is, its inflammation is difficult.

2.3.2 Vertical Burning Test

50mm × 52mm sample provided in the lit burner was placed, after the provisions of ignition time, the measurement of the sample were flame burning time, flameless Combustion time, flame length damaged, the percentage of weight loss[4]. The smaller the value of these parameters is the better that anti-fire of leather is.

2.3.3 Smoke Density

According to the national standard GB/T8627-1999 "combustion or decomposition of building materials of the smoke density of the experimental method" [5], the method is served for detection of smoke density leather. In the course of test, smoke was produced Sample combustion in the box in order to measure Parallel beam through the smoke of the transmittance change and Obtain Optical density. Sample of per unit area is generated by the proliferation of tobacco smoke in the unit box unit of volume of smoke optical density.

2.4 The Test Method of Fat Content

Soxhlet extraction method was utilized [6] in order to measure the changes in fat content before and after fat liquoring.

2.5 Sensory Indicators of Leather

2.5.1 Feel and Fullness

The leather handle and Fullness is made use of contrast-scoring, scores from 1 ~ 10 minutes. Blank samples and test samples were evaluated by this method.

2.5.2 Flexibility

HZ-3004 testing machine flexibility (based on IULTC IUP/36, ISO17235-2002) was used for leather

softness. Choosing at least three samples of different parts of the leather and placing static test specimen on the temperature at 21 ℃ and Relative humidity of 65% can be measured when time is over 24h.

2.6 Determination of Thickness

Scheduled to re-type thickness browser can be measure thickness of leather ranged from 0～10mm, 0.01mm of precision[7].

3 Results and discussion

3.1 Screening Fatliquor

3.1. 1 Changes of Oil in Leather

Tab. 1 Influence on the absorption of fatliquor for flame retardant

Flame retardant	Fatliquor	Fat content in leather (%)	Amount of oil in leather (%)	Rate of increase oil of leather (%)
Blank	SE	6.44		
	NC	2.06		
	ME	5.22		
	NLM	5.47		
KZR-2	SE	12.12	5.68	88.20
	NC	8.23	6.17	299.51
	ME	18.41	13.19	252.68
	NLM	8.84	3.37	61.61
SC-968	SE	11.92	5.48	85.09
	NC	10.74	8.68	166.28
	ME	13.69	8.47	162.26
	NLM	9.17	3.70	67.64
FR-102	SE	9.20	2.76	42.86
	NC	7.64	5.58	270.87
	ME	10.12	4.90	93.87
	NLM	8.41	2.94	53.75

It can be found from Tab. 1 that flame retardants fatliquoring imposed flame retardants KZR-2, SC-968, FR-102 on fat emulsion in fatliquoring Section can significantly improve specific Absorption Rate of four types of SE, NC, ME, MLM Fatliquor in leather. And KZR-2 can promote the absorption of four kinds of fat in most obvious effect, SC-968 out second, FR-102 was located in the final. Under KZR-2, grease of NC fatliquor from leather was in the largest rate of increase, ME came in second, SE third. At the same time, under the influence of KZR-2, grease of leather made from four types of oils and fats, ME greatest, SE came in second place.

3.1.2 Sensory Changes of Leather

It can found from experimental data of Tab. 2 that three types of flame retardants will promote

flexibility of leather. And flame retardant will not lower leather feel and fullness that traditional flame retardant gave rise to. SC-968 can promote most soft, followed by KZR-2, the final FR-102.And three types of flame retardants SC-968, KZR-2, FR-102 will promote or not reduce feel and fullness of Fatliquor SE leather.

Tab. 2 Influence on sensory properties of different types of fatliquor for flame retardant

Flame retardant	Fatliquor	Thickness (mm)	Flexibility	Feel	Fullness
Blank	SE	0.875	7.90	9	More
	NC	0.885	6.99	5	More
	ME	0.843	6.73	7	More
	NLM	0.883	6.36	3	Good
KZR-2	SE	0.883	8.31	9	Most
	NC	0.816	8.17	5	More
	ME	0.794	8.02	8	Good
	NLM	0.771	8.38	2	Most
SC-968	SE	0.684	9.17	9	More
	NC	0.715	8.77	4	Most
	ME	0.724	8.50	6	More
	NLM	0.819	8.47	2	Good
FR-102	SE	0.824	8.12	9	Most
	NC	0.782	7.68	6	Good
	ME	0.910	7.63	1	More
	NLM	0.866	7.49	4	More

3.1.3 Flame-Retardant Properties of Fatliquor Leather

From Tab. 3, it can be found that leather made in KZR-2, SC-968, and FR-102 in fat emulsion released small smoke volume when it burned. And three types of flame retardants on the leather of the smoke released by burning were basically the same. Under certain conditions, three types of flame retardants had a certain degree of smoke suppression. Another an important indicator oxygen index of leather flame retardancy can be found that KZR-2 of four types of leather fatliquor on oxygen index was increased very significantly and synthesis fatliquor SE and sulfuric acid fish oil NC influenced on KZR-2 that will enable the synthesis SE fatliquor leather reach at the level of non-combustible was particularly in oxygen index (textile provides oxygen index less than or equal to 21, for the combustible ,21-28 for fuel, 28-32 between the flame retardant material, more than 32 non-combustible material). And SC-968 can increase oxygen index of leather, but less than KZR-2. FR-102 of leather can increase oxygen index between the SC-968 and FR-102. FR-102 can help fish oil the minimum oxygen index. SE fatliquor influenced on three flame retardants had shown that the best or better fire-retardant effect. Other fatliquor leather owned anti-incombustibility less.

Comparison of absorption rate, feel, fullness, softness, oxygen index, smoke density, flame retardant

can help SE improve grease of leather and own good anti-incombustibility comparated with other fatliquor. Four orders of four kinds of fatliquor on KZR-2 of incombustibility are SE, NC, NLM, and ME. So SE and KZR-2 were selected for screening flame retardant.

Tab. 3 Different types of flame-retardant properties of leather fatliquor

	Fatliquor	Smoke density	Oxygen index (%)	Increase the amount of oxygen index (%)
Blank	SE	9	24.3	
	NC	8	25.2	
	ME	8	24.7	
	NLM	7	24.2	
KZR-2	SE	2	31.6	7.3
	NC	5	31.5	6.3
	ME	6	29.7	5.0
	NLM	4	29.8	5.6
SC-968	SE	4	28.8	4.5
	NC	1	27.9	2.7
	ME	2	27.6	2.9
	NLM	4	27.4	3.2
FR-102	SE	2	28.7	4.4
	NC	5	26.8	1.6
	ME	4	28.2	3.5
	NLM	1	28.9	4.7

3.2 Flame Retardant KZR-2

3.2.1 Changes of Oil in Leather

Tab. 4 Flame retardant KZR-2 influence on grease of leather

KZR-2 dose (%)	Fat content in leather (%)	Increasing volume of grease (%)	Increased rate of oil of leather (%)
0	12.75		
0.5	12.97	0.22	1.73
1	26.92	14.17	111.13
1.5	18.42	5.67	44.47
2	12.95	0.20	1.57
3	13.99	1.24	9.73
6	24.96	12.21	95.76
9	21.43	8.68	68.08
12	21.53	8.78	68.86
15	21.73	8.98	70.43

On the basis of SE, leather fatliquor SE was selected for KZR-2 from Tab. 4. It was found that grease of leather was all more than grease of leather without flame retardant with the increase of dose of flame retardant. The growth rate of fatliquor in leather was respectively 111.13%, 95.76%, 68.08% when flame retardant KZR-2 was put leather in dose of 1%,6%,9%.and content of 1% KZR-2 will enable the fat content of leather significantly increased, up to more than 100%.

3.2.2 Sensory Changes of Leather

Tab. 5 Influence on sensory properties for flame retardant in leather

KZR-2 dose/%	Flexibility	Thickness(mm)	Feel	Fullness
0	7.83	0.788	5	More
0.5	8.04	0.786	9	More
1	7.95	0.887	9	More
1.5	8.30	0.850	8	Most
2	8.36	0.776	7	More
3	8.02	0.831	6	More
6	8.17	0.834	3	More
9	7.93	0.844	2	More
12	7.94	0.845	3	More
15	7.96	0.851	2	More

It was found from Tab. 5 that flexibility of leather was all more than flexibility of leather without flame retardant with the increase of dose of flame retardant. The softness of the leather was best when dose of flame retardant was 2%. And thickness of leather imposed on flame retardant was bigger than thickness of leather without flame retardant. When amount of flame retardant was 1%, the increase in the thickness of the leather was the largest. Imposed by the volume of flame retardant of 0.5% and 2%, although reduce the thickness of the leather was slightly reduced, but the reduction was in the error range. Imposed in 0.5% and 1% of flame retardant, leather feel was the best. Fullness of leather was not much change with the increase of dose of flame retardant.

3.2.3 Flame-Retardant Properties of Fatliquor Leather

3.2.3.1 Vertical Combustion

Under normal circumstances, loss of length and weight loss were the same with the increase of dose of flame retardant. Flame burning time of leather was relatively short than leather without flame retardant. That flame retardants in the leather ahead of leather combustion and cross-linked of leather proteins prevented the possibility of combustion.

Flameless combustion time and flame combustion time without flame retardant were also long. Flameless combustion time of leather was small than leather without flame retardant. But flameless combustion time of 6% in leather was longer than blank. This was the reason that the flame can be transformed into flameless combustion under certain conditions. Therefore, evaluation of materials should be considered the flame combustion time and flameless Combustion time. Flame combustion time was biggest when 6%. Flame combustion time and flameless Combustion time was also small when 2%. So burning time was the shortest burning time of 1.5% was second.

Tab. 6 Influence on vertical combustion of leather for KZR-2

Amount of flame retardants (%)	Flame burning time (s)	Flameless Combustion time (s)	Loss of length (cm)	Percentage of weight loss(%)
0	135.8	417.6	24.0	57.6
0.5	2.3	36.5	1.1	1.9
1	8.3	33.1	2.2	3.5
1.5	2.7	27.5	2.3	3.0
2	3.8	24.6	1.4	2.3
3	116.1	5.7	21.2	37.3
6	66.6	687.9	24.3	58.8
9	28.6	17.5	8.2	7.7
12	122.5	233	24.2	43.0
15	29.9	5.3	14.1	11.8

3.2.3.2 Oxygen Index

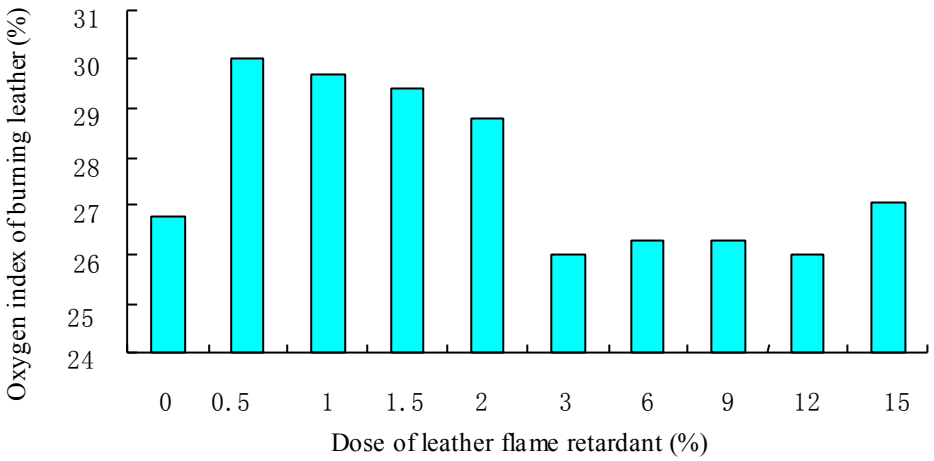

Fig.1 Influence on oxygen index for leather flame retardant KZR-2

With the increase of dose of flame retardant, oxygen index leather was greater when 0.5%～2%. The absorption of oil and fat of leather was increased firstly and then decreased again increased and then reduced. Grease of leather was in a high level when 1.0%～1.5%. Absorption rate of leather made in 1.0%~1.5% flame retardant was bigger and flexibility was high level when1.5%～2.0% flame retardant.

3.2.3.3 Smoke Density

With the increase of dose of flame retardant, smoke density of leather without flame retardant was smaller than leather with flame retardant. In the light of flame burning time and burning time, burning a lot of fire without flame retardant of leather brought about small smoke.

Comparing with weight loss of burning materials, loss of length, burn time (with flame combustion and flameless combustion), oxygen index, smoke density, oil absorption rate and the flexibility, 1.5% KZR-2 of leather possessed flame-retardant properties the absorption rate of the oil softness.

Therefore, comparison can be drawn when the flame retardant selected 1.5% KZR-2, leather flame

time, damage to the length, the weight loss percentage, smoke density, oxygen index, the absorption rate of the oils and fats as well as the flexibility taken together, showed the best results.

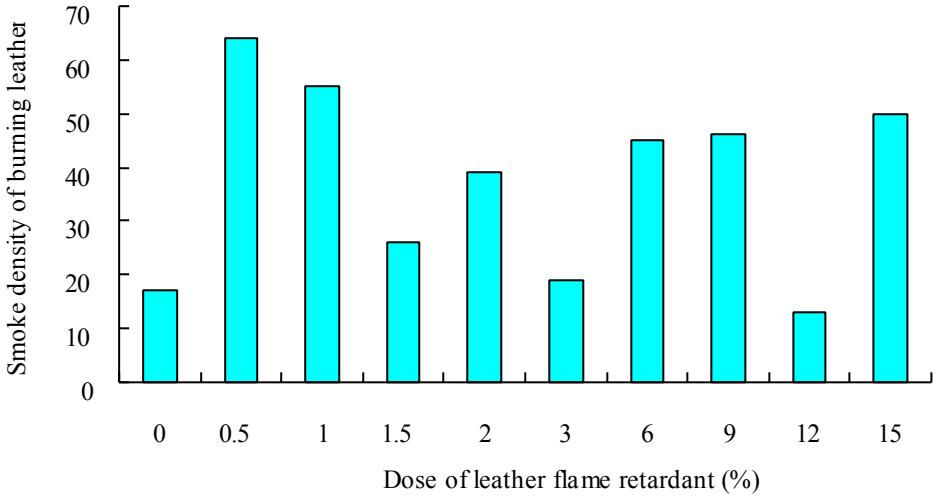

Fig. 2 Influence on smoke density for leather flame retardant KZR-2

4 Conclusions

Three types of flame retardants KZR-2, SC-968, FR-102 can enhance absorption of the different types of leather Fat liquor (synthetic, sulfated oil, sulfated castor oil, phospholipids). Comparison of absorption rate, feel, fullness, softness, oxygen index, smoke density, three flame retardants can help leather absorb fat content of SE and make SE leather contain best anti-incombustibility of fatliquoring leather. And anti incombustibility order of four fatliquor successively was SE, NC, NLM, and ME. SE was screened for fatliquor of the main section

Comparison can be drawn when the flame retardant selected 1.5% KZR-2, leather flame time, damage to the length, the weight loss percentage, smoke density, oxygen index, the absorption rate of the oils and fats as well as the flexibility taken together, showed the best results.

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