

COMPARISON OF FINISHING APPLICATION FOR ALIPHATIC POLYURETHANE DISPERSIONS AND POLYURETHANE/POLYACRYLATE COMPOSITE EMULSIONS*

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ABSTRACT

Aliphatic and aromatic cationic aqueous polyurethane (PU-1, PU-2), aliphatic anionic aqueous polyurethanes (PU-3, PU-4) were prepared with polyether glycol, polyether polyol, toluene diisocyanate and isophorone diisocyanate as raw materials. The core-shell polyurethane/polyacrylate composite emulsions (PUA-5, PUA-6) as well as interpenetrating PUA composite emulsions (PUA-7, PUA-8) were prepared by seeded emulsion polymerization, the aliphatic anionic aqueous PU dispersions were used as seed particles, glycidyl methacrylate was used as the bridge of core and shell in second stage polymerization. A study using different finishing applications for pigskin garment leather was carried out with the aliphatic anionic PU dispersion, the core-shell and interpenetrating structure PUA hybrid emulsions as film forming agents. The wet rub fastness, solvent resistance, flex resistance, adhesive fastness of the coating in finished leather were measured respectively. The results are as follows: (1) the anionic PU dispersions, the core-shell and interpenetrating PUA composite emulsions showed good film forming, good covering grain damage and mending properties, and strong adhesive force to leather. The finished leathers were soft, flat, smooth, non-sticky and their grain patterns were clear; (2) The interpenetrating PUA is better than core-shell PUA and the core-shell PUA is better than the PU dispersion at wet rub fastness, solvent resistance, adhesive resistance. Both PU dispersion and core-shell PUA were better than the interpenetrating PUA at flex resistance by comparison.

RESUMEN

Poliuretanos acuosos catiónicos alifáticos y aromáticos (PU-1, PU-2) y poliuretanos acuosos aniónicos alifáticos (PU-3, PU-4) fueron preparados con polieterglicol, polieterpoliol, diisocianato de tolueno y diisocianato de isoforona como materias primas. El núcleo de la emulsión del compuesto poliuretano/poliacrilato (PUA-5, PUA-6), así como la emulsión del compuesto interpenetrante PUA (PUA-7, PUA-8) fueron preparadas por polimerización de la emulsión semilla, la dispersión acuosa del poliuretano alifático aniónico fue utilizada como partícula de semilla, metacrilato de glicidilo fue utilizado como puente del núcleo y como cubierta en la polimerización de la segunda etapa. Un estudio basado en las diferentes aplicaciones de acabado de cuero de piel de cerdo para vestimenta se llevó a cabo con la dispersión de poliuretano aniónico alifático y la emulsión híbrida del núcleo-recubierto y la emulsión compuesta interpenetrante PUA como agentes formadores de película. La solidez a los frotos húmedos, la resistencia a los disolventes, la resistencia a la flexión, la solidez a la adhesión del acabado en el cuero terminado fueron respectivamente medidos. Los resultados son los siguientes: (1) la dispersión de poliuretanos aniónicos, la emulsión híbrida del núcleo-recubierto y la emulsión compuesta interpenetrante PUA mostraron buena formación de película, buena cobertura de defectos de flor así como buenas propiedades de reparación, y una fuerte adhesividad al cuero. Los cueros acabados fueron blandos, lisos, suaves, no pegajosos y los rastros de flor fueron distinguibles; (2) El interpenetrante PUA es mejor que la del núcleo-recubierto PUA y el núcleo-recubierto PUA es mejor que la dispersión de PU en cuanto a la solidez a los frotos húmedos, en la resistencia a los disolventes y en la adhesividad. Tanto la dispersión de PU y el núcleo-recubierto PUA fueron mejores en comparación con el interpenetrante PUA, en la resistencia a la flexión.

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INTRODUCTION

Acrylic polymer emulsions (PA) have been widely used for leather coatings. Interest in polyurethane dispersions (PU) has increased in the last decade because they are environmentally friendly materials.¹⁻³

Acrylic polymer emulsions and polyurethane dispersions each have their own characteristic advantages and disadvantages.⁴ Physical blends of the two polymer systems are a popular approach to combine the beneficial attributes of each polymer. However in many cases these blends compromise the superior performance properties because of the incompatibility of the two systems.⁵ A way to achieve the best properties of both systems is to synthesize the polyurethane/polyacrylate (PUA) composite latex particles. In these systems, the PU dispersion is used as a seed for subsequent radical emulsion polymerization, resulting in intimately mixed composite particles; that is, both polymers are present in a single latex particle and form core-shell structure.⁵ If one of the polymers is a crosslinked structure, the composite polymer will form latex interpenetrating polymer networks (i.e., LIPN). LIPN is a special structural core-shell latex. LIPN also belongs to interpenetrating polymer networks (IPNs) which are defined as blends of two or more polymers networks where at least one polymer component is prepared or crosslinked in the immediate presence of others. The polymer networks are physically entangled with each other or at least partially interlaced on a molecular scale and cannot be separated unless chemical bonds are broken. A mixture of two or more preformed polymer networks is not an IPN. Besides ideal or full IPNs, in which both components are crosslinked independently of each other, there are also other types of IPNs such as semi-IPNs or grafted-IPNs. Semi-IPNs have only one component cross-linked, while grafted-IPNs have covalent cross-links between both networks.⁶ Whichever IPNs it is, it could reveal "forced miscibility and coordinated effect" and lead to outstanding comprehensive properties. In a word, because of the unique core-shell and interpenetrating network structures, the core-shell and LIPN techniques have been widely practiced in recent years.⁷⁻⁹

Although there have been some reports demonstrating the benefit of core-shell type composite emulsions, most of them used the aromatic diisocyanates as raw materials and are still in the stage of experiments, and have not been industrialized in leather production. The core-shell PUA composite emulsions using the aliphatic diisocyanates as raw materials are limited.⁴ With regard to the crosslinked or IPN composite PUA, most reports are as follows: (1) PU prepolymers are prepared with isocyanate end groups, then the composite PUA emulsions are synthesized by using the unsaturated carbon-carbon bond monomers, such as hydroxyethyl methacrylate, hydroxypropyl methacrylate, maleic anhydride,

fumaric acid, methacrylic anhydride as the bridge of the copolymerization reactions. (2) The hydrazine group is introduced into the shell part, it then reacts with the ketone group in diacetone acrylamide that is one of the core monomers, then another crosslinking reaction can take place between the core and shell.^{4,10}

Till now, there are few reports concerning the composite PUA emulsion prepared by adding glycidyl methacrylate in the second stage polymerization and crosslinked by the chemical reaction between epoxy group and imino, carboxyl group in the polyurethane molecule chains. In our previous study, anionic aqueous polyurethane dispersion was prepared using a carboxyl acid group to make the polyurethane dispersible,¹¹ and then nanograde core-shell and interpenetrating PUA composite latex were synthesized by a soap-free emulsion polymerization method with PU dispersion as the seed. FTIR, DSC, dynamic light scattering, TEM, X-ray photoelectron spectroscopy (ESCA), TGA, electronic tensile machine were employed to investigate the structure and properties of the composite latex and their polymers.¹²

Finishing is one of the main processes for the preparation of leather. The application results of the aqueous PU dispersions and PUA composite emulsions are affected not only by the properties of the PU dispersions and PUA emulsions, but also by the coating conditions. Tanners usually care very much about the properties of the coating on the surface of leather, such as softness, touch, toughness, covering grain damage and mending properties, adhesive force to leather, wet fastness, solvent resistance, flex resistance.¹³⁻¹⁴ This article mainly focuses on the study of finishing applications using aliphatic PU dispersions and PUA composite emulsions.

EXPERIMENTAL

Synthesis Part

Materials

Toluene diisocyanate(TDI) was chemical grade and was supplied by Peking Xizhong Chemical Plant, isophorone diisocyanate(IPDI) was supplied by Hues AG Company in Germany, polypropylene glycol (PPG-1000, PPG-2000), polypropylene polyol (PPG-3000) were supplied by the 3rd Petrochemical Plant of Tianjin, glycidyl methacrylate (GMA) was supplied by Suzhou Anli Chemical Factory. Dibutyltin diurate(T-12), dioctyl phthalate(DOP), acetone, N-methyldiethanolamine(N-MDEA), ice acetic acid(AA), dimethylolpropionic acid (DMPA), triethyl amine (TEA), 1,4-butanediol (BDO), potassium persulfate (KPS), methyl acrylate (MA), butyl acrylate (BA), sodiumdodecylsulfate (SDS) were purchased from Peking Chemical Reagent Company.

PPG was dried at 70 °C, 0.1mm Hg for 72h before use. The acetone, DOP and BDO were used after treating with 4A molecular sieves for 72h. IPDI, MA, BA, GMA were distilled respectively under reduced pressure. DMPA, KPS, TEA, T-12, SDS, N-MDEA, AA were analytically pure grade, and were used as received, water was deionized and distilled, the conductivity of which was below 1µs /cm.

Synthesis of the aliphatic and aromatic cationic aqueous polyurethane dispersions

The synthesis of the aliphatic and aromatic cationic aqueous polyurethane dispersions were carried out in a four-neck glass reactor equipped with a mechanical stirrer, a thermometer, a nitrogen inlet. First, IPDI (or TDI), PPG and few of drops T-12 of DOP solution were poured into the reactor, the reactor mixture was kept 90°C for about 3 h, until the NCO% dropped below theoretical values, the reactor was cooled down to 50°C, freshly dried acetone was added into it in order to bring down the viscosity of these polyurethane prepolymer. The N-MDEA was added and temperature remained constant for another 1 h. Then, The polyurethane dispersion was obtained from a high shear rate mixing of this polyurethane prepolymer with aqueous solution of acetic acid after acetone were removed by vacuum. The recipe is summarized in Table I.

Synthesis of the Aliphatic Anionic Aqueous Polyurethane Dispersions

The synthesis of the aliphatic anionic aqueous polyurethane dispersions was also carried out in a four-necked glass reactor. First, IPDI, PPG, DMPA and a few drops of T-12 of DOP solution were poured into the reactor, and the reaction mixture was kept at 80 °C for about 3 h, until the NCO% dropped below 3.0. BDO was added and the temperature remained constant for another 1 h. Then, the reactor was

cooled down to 40-45 °C, to which freshly dried acetone was added in order to bring down the viscosity of these PU prepolymers. The PU dispersions were obtained from a high shear rate mixing of these PU prepolymers with aqueous solution of TEA after acetone was removed under vacuum. The recipes are summarized in Table II.

Preparation of Core-shell and Crosslinked PUA Composite Emulsions

The core-shell and crosslinked PUA composite emulsions were prepared by soap-free seeded emulsion polymerization with the above-synthesized anionic aqueous PU dispersion as seed particles. The mixture of MA and BA were used in the second stage polymerization for core-shell PUA, the mixture of MA, BA, GMA were used in the second stage polymerization for crosslinked PUA. The second-stage soap-free seeded emulsion polymerization was carried out with KPS as initiator at 80°C for 4h. Table III shows the recipes used in the preparation of the PUA composite emulsion.

It should be noted that we numbered the synthesized PU as well as PUA using the names (PU-1, PU-2, PU-3, PU-4, PUA-5, PUA-6, PUA-7, PUA-8) for convenience. The main properties of the PU dispersions and PUA emulsions are shown in Table IV. The methods of the preparation were also shown in references.¹¹⁻¹²

Finishing experiments

Materials

Twelve (4×3=12, the following 4 schemes were carried out in triplicate) pigskin garment leather crusts were used for finishing experiments. The pigskin garment leather crusts were supplied by Yi Yuan Leather Factory (Shandong,

TABLE I
The Mole Ratios of the Cationic Polyurethane Dispersion Recipes

Reagents	PPG-1000	PPG-3000	N-MDEA	TDI	IPDI	AA
PU-1	0.035	0.0023	0.07-0.12		0.15	0.07-0.12
PU-2	0.035	0.0023	0.07-0.12	0.15		0.07-0.12

TABLE II
The Mole Ratios of the Anionic Polyurethane Dispersion Recipes

Reagents	IPDI	PPG-1000	PPG-2000	BDO	DMPA
PU-3	0.30	0.0525	0.0525	0.08-0.2	0.06-0.10
PU-4	0.30	0.0475	0.0475	0.08-0.2	0.10-0.14

TABLE III
Recipes for Core-Shell and Crosslinked PUA Composite Emulsions

PUA samples	PU seed(g)		second-stage polymer			K ₂ S ₂ O ₈ (g)	H ₂ O(g)
	PU-3	PU-4	MA(g)	BA(g)	GMA(%)		
Core-shell PUA-5	25		3.75	3.75	0.0	0.03-0.05	28.0
Core-shell PUA-6		25	3.75	3.75	0.0	0.03-0.05	28.0
Core-shell PUA-7	25		3.75	3.75	2-4	0.03-0.05	28.0
Core-shell PUA-8		25	3.75	3.75	2-4	0.03-0.05	28.0

GMA% is based on the total acrylate mixture monomers

TABLE IV
The Main Properties of the PU Dispersions and PUA Composite Emulsions

Products	PU-1	PU-2	PU-3	PU-4	PUA-5	PUA-6	PUA-7	PUA-8
Solid content (w/w%)	30.5	31.3	30.8	29.1	31.7	30.4	29.7	30.0
pH value	7.5	7.8	8.6	8.3	8.5	8.6	8.5	8.2
Appearance	dispersion	dispersion	dispersion	dispersion	emulsion	emulsion	emulsion	emulsion
Storage stability	half year	half year	one year	one year	half year	half year	half year	half year
Thermal stability	stable	stable	stable	stable	stable	stable	stable	stable
Film forming property	/	/	good	good	good	good	good	good
Type	aliphatic cationic	aromatic cationic	anionic linear	anionic linear	anionic core-shell	anionic core-shell	anionic interpenetrating	anionic interpenetrating

TABLE V
Sealing Coat Formulations Used for Pigskin Garment Leathers

Scheme	1	2	3	4
Aliphatic cationic PU dispersion (PU-1)				180
Aromatic cationic PU dispersion (PU-2)	180	180	180	
Water	280	280	280	280

TABLE VI
Base Coat Formulations of Pigskin Garment Leathers for Scheme 1, 2, 3, 4

Scheme	1	2	3	4
Black pigment	100	100	100	
White pigment				100
Water	300	300	300	300
Anionic polyurethane dispersion (PU-3)	120			
Anionic polyurethane dispersion (PU-4)	80			
Core-shell PUA composite emulsion (PUA-5)		120		
Core-shell PUA composite emulsion (PUA-6)		80		
Interpenetrating PUA composite emulsion (PUA-7)			120	120
Interpenetrating PUA composite emulsion (PUA-8)			80	80
Acrylic binder XG-461	20	20	15	20

TABLE VII
Color Coat Formulations of Pigskin Garment Leathers for Scheme 1, 2, 3, 4

Scheme	1	2	3	4
Black pigment	100	100	100	
White pigment				100
Water	300	300	300	300
Anionic polyurethane dispersion (PU-3)	80			
Anionic polyurethane dispersion (PU-4)	120			
Core-shell PUA composite emulsion (PUA-5)		80		
Core-shell PUA composite emulsion (PUA-6)		120		
Interpenetrating PUA composite emulsion (PUA-7)			80	80
Interpenetrating PUA composite emulsion (PUA-8)			120	120
Anionic silicon-containing agent	10	10	10	10
Anionic wax emulsion	100	100	100	100

TABLE VIII
Top Coat Formulations of Pigskin Garment Leathers for Scheme 1, 2, 3, 4

Component	Parts of component
Cellulose nitrate bright component	100
Anionic wax emulsion	10
Anionic silicon-containing agent	20
Water	100

China). The black pigment and the white pigment were supplied by Shanghai Gold Lion Leather Finishing Factory (Shanghai, China). Acrylic binder XG-461 and the anionic wax emulsion (WE-B) were from Chengdu Organic Chemicals CO., LTD., Chinese Academy of Sciences (Chengdu, China). The cellulose nitrate bright component (No 745) was supplied by Tianjin Jufeng Leather Chemical Co., LTD (Tianjin, China). The anionic silicon-containing agent was supplied by Hangzhou Tongda Leather Chemical Co., LTD. (Hangzhou, China). All materials used for finishing leather were industrial grade.

TABLE IX
Results of Dry and Wet Rub Fastness of the Finished Leathers

Finishing system		Aliphatic PU	Core-shell PUA	Interpenetrating PUA	Interpenetrating PUA
Scheme		1	2	3	4
Color		black	black	black	white
Dry rub fastness	Standard value	≥4.0	≥4.0	≥4.0	≥4.0
	Measured value	4.0	4.5	5.0	5.0
Wet rub fastness	Standard value	≥3.0	≥3.0	≥3.0	≥3.0
	Measured value	3.0	4.0	4.5	4.5

TABLE X
Methyl Ethyl Ketone Rub Resistance of Finished Leather Coatings

Finishing system	Aliphatic PU	Core-shell PUA	Interpenetrating PUA	Interpenetrating PUA
Scheme	1	2	3	4
Rub cycles with methyl ethyl ketone	5	300	500	500

TABLE XI
Adhesive Strength of Finished Leather Coatings in Dry and Wet State in Short Time

Finishing system	Aliphatic PU	Core-shell PUA	Interpenetrating PUA	Interpenetrating PUA
Scheme	1	2	3	4
Peel strength(N/mm) and phenomena in dry state	1.5	1.6	1.6	1.6
	Grain side is broken	Grain side is broken	Grain side is broken	Grain side is broken
Peel strength(N/mm) and phenomena in wet state	0.22	0.35	0.56	0.5
	Coatings peel off	Coatings peel off	Coatings peel off	Coatings peel off
Peel strength(N/mm) and phenomena in toluene in short time	0	0.22	0.34	0.37
	Coatings dissolve	Coatings peel off	Coatings peel off	Coatings peel off

TABLE XII
Flex Resistance of the Finished Leather Coatings

Finishing system	Aliphatic PU	Core-shell PUA	Interpenetrating PUA	Interpenetrating PUA
Scheme	1	2	3	4
Flexing cycles when coatings occur crease	20000	20000	15000	15000
Final flexing cycles	50000	50000	45000	45000

TABLE XIII
Touch Properties of the finished leather

Finishing system	Aliphatic PU	Core-shell PUA	Interpenetrating PUA	Interpenetrating PUA
Scheme	1	2	3	4
Smoothness	smooth	smooth	smooth	smooth
Stickiness	nonsticky	nonsticky	nonsticky	nonsticky
Softness(mm)	0.52	0.39	0.285	0.285
Grain pattern	clear	clear	clear	clear

Formulations and procedures of the finishing experiments

The aqueous PU dispersions are widely used in the leather finishing system, but most of the aqueous PU used in leather finishing is the anionic type. The final finished leathers have excellent properties, but also have some disadvantages. One of them is that the anionic dispersions can easily be absorbed by the leather, so the fullness and touch feeling of the leather is not very good. Another disadvantage is that there are some hydrophilic groups such as carboxyl group in the molecule chains, so the wet rub resistance of the finished leather is lower. A new type of film forming core-shell and interpenetrating PUA emulsions can solve these problems.

In our work, based on the synthesized anionic PU dispersions and core-shell PUA composite emulsions, the finishing operations were carried out. Scheme 1, 2, 3 (for black leathers) correspond to the anionic PU dispersion, core-shell and interpenetrating PUA composite emulsions respectively. The interpenetrating PUA emulsion finishing system for white leather (scheme 4) is also used for contrast. The sealing coat, base coat, color coat, top coat formulations are shown in Table V, Table VI, Table VII, Table VIII, respectively. The top coat formulations are for scheme 1, 2, 3 4. The finishing conditions and finishing procedures were the same with the regular production in Yi Yuan Leather Factory in China.

Test methods for the finished leathers

Wet rub fastness

Wet rub fastness was conducted using a rub fastness tester GJ9G-1 made by Zhejiang Yuyao Industry Machinery (Zhejiang, China). A felt rubbing pad was saturated with water and placed on the equipment rubbing head, the leather swatch was inserted into the rub fastness tester, the water saturated felt pad was applied to the finished surface and 100 rubbing cycles were completed. The color difference between the felt pads was assessed using a grayscale chart.

Solvent resistance of the coatings

The measurement method of solvent resistance of the coatings imitated the wet rub fastness. A felt rubbing pad was saturated with methyl ethyl ketone instead of water. In the process of rubbing, the methyl ethyl ketone was supplemented in order to keep the leather surface wet.

Flex resistance

A swatch of the finished leather was attached to a flexometer (GJ9C-1) made by Zhejiang Yuyao Industry Machinery (Zhejiang, China) according to GB4689.9-84.¹⁵ The bending angle is 20°30', the flexing rate is 100 times per minute. The changes of the coatings were observed every 5000 flexing cycles with a magnifying glass (the multiple is 6x). The final cycle times were taken down when the coatings have not shown any cracking or white crazing.

Adhesive force to leather

A leather swatch was cut into a strip, 25 mm wide and 150 mm long. One end was fixed on the 25 mm wide aluminum patch using epoxy resin and cured for 24 hours at ambient temperature. The peel strength and peel phenomenon were measured at a crosshead speed of 100mm/min using a XL-50A tensile machine made by Guangzhou Testing Instrument Factory (Guangzhou, China). After inserting the solidified leather swatch in water for 12 hours, the wet peel strengths were measured. After dipping the solidified leather in toluene for two minutes, the peel strength of the coatings in solvents for two minutes was measured too.

Softness of the finished leather

The softness of the finished leather was measured with a softness tester made by Tonny International Co. LTD (Guangdong, China). The unit of the softness is millimeter(mm). The bigger the value is, the softer the finished leather.

Touch feeling of the finished leather

A subjective assessment of the finished leather was conducted by feeling the leather in multiple ways. To assess the touch

feeling of the finished leather, the leather surface was evaluated by rubbing the surface and measuring level of smoothness, stickiness and observing the grain surface.

RESULTS AND DISCUSSION

Dry and wet rub fastness of finished leather

According to industry standard QB1872-93,¹⁶ the dry and wet rub properties were measured, the results are shown in Table IX. The standard values of dry and wet rub fastness of the finished pigskin garment leathers were 4 and 3, respectively. The measured values of dry and wet rub fastness of the finished pigskin garment leathers were over 4 and 3, respectively. They were all up to standard.

The dry and wet rub resistances about the finished leather with the interpenetrating PUA composite emulsions as film forming materials are better than using the core-shell PUA composite emulsions. The dry and wet rub resistance of the finished leather using the core-shell PUA composite emulsions is better than using the anionic PU dispersion from Table IX.

Solvent type polyurethane has an excellent abrasion resistance feature. However, in the process of preparation of the aqueous polyurethane, the carboxyl acid groups were introduced in the polymer chains which had high hydrophilic properties. The coatings on leather will swell when in contact with water and the mechanical strength will also decrease greatly. The wet rub fastness will also be affected.

In the process of preparation of the core-shell PUA composite emulsions, acrylate groups were introduced, the contents of the carboxyl acid groups in PUA system decreased largely, the wet rub resistance of the finished leather using the core-shell PUA as film forming materials was better than using the aqueous PU dispersion. In the process of preparation of the interpenetrating PUA, the epoxy groups were introduced in the polymer chains. The epoxy group can react with the carboxyl acid group and the hydrophilic property can be eliminated by controlling the contents of the epoxy group in PUA chains. So the wet rub resistance of the finished leather using interpenetrating PUA as film forming materials was the best.

Solvent resistance of finished leather coatings

A linear polyurethane or polyacrylate can dissolve in methyl ethyl ketone or acetone. Hybrid or interpenetrating PUA only can swell in the organic solvent and maintains certain mechanical strength. There usually a small chance that organic solvent will come in contact with the normal use of leather. However, in the process of producing leather products such as leather shoes, leathers need to cement to soles with an adhesion agent which may contain some

organic solvents. The leather coatings can possibly peel off the leather from the action of the organic solvent. Till now, there is no a standard method characterizing the solvent resistance of the leather coatings in China. According to the principle of methyl ethyl ketone rub resistance of coatings in the painting industry, together with dry and wet rub fastness instruments in the leather industry, the forward and backward rubbing cycle times were measured, when the leather coatings were totally broken in the action of the methyl ethyl ketone. And the changes of the peel strength in the action of methyl ethyl ketone were used to characterize the organic solvent resistance of the leather coatings. Table X shows the results of solvent resistance of the leather coatings. The finished leather using the aliphatic aqueous PU finishing system only can bear 5 times of methyl ethyl ketone rub. The finished leather using the core-shell PUA finishing system can withstand 300 times. The finished leather using the interpenetrating PUA finishing system can bear 500 times.

Table XI lists the results of the changes of the finished leather coatings in action of methyl ethyl ketone rub. The finished leather coatings using PU finishing system dissolved in toluene in short time. The finished leather coatings using core-shell PUA finishing system can withstand the action of toluene in short time and has certain mechanical strength. The finished leather coatings using interpenetrating PUA finishing system can withstand the action of toluene for a short time and has stronger mechanical strength. In a word, the interpenetrating structure can increase the solvent resistance of the leather coatings greatly as shown in Table X and XI.

Flex resistance of the finished leather coatings

Usually, the tensile strength of the composite polymers increases, the elongation at break decreases after crosslinking. The changes of these properties possibly affect the flex resistance of the finished leather coatings. Table XII shows the results of flex resistance of different finished leather coatings. The aliphatic PU coatings and the core-shell PUA coatings did not show cracking or white crazing after 50000 flexing cycles. The interpenetrating PUA did not show cracking or white crazing after 45000 flexing cycles. Although the flex resistance of the interpenetrating PUA coatings is slightly lower, the materials exceed greatly the national standard.

Adhesive strength of the finished leather coatings

There are three kinds of forces that will affect the adhesive strength between coatings and leather base. They are physical adsorption force, intermolecular force between interfaces and chemical bonding force. In general, the physical adsorption force and intermolecular force contribute a lot to the adhesive strength of the leather base and coatings. But the chemical bonding force plays an important part in resisting media such as water abrasion. Table XI shows the

peel strengths of the finished leather coatings in dry state and dipping in water for 12 hours. Different types of coatings had the same dry peel strength. At this moment, the peeling appeared in the form of broken grain side. The actual adhesive strengths of the coatings were higher than this value. In wet state, the interpenetrating PUA coatings had the highest adhesive strength, the aliphatic aqueous PU had the lowest adhesive strength, core-shell PUA coatings were in-between. This is possibly correlative with whether or not there are crosslinking and the degree of the crosslinking.

Touch feeling of the finished leather

The touch feeling of the finished leather are shown in Table XIII. All the finished leathers are flat, smooth, non-sticky and their grain patterns are clear. The finished leather using PU finishing system is the softest, the finished leather using the interpenetrating PUA system is the hardest. The finished leather using core-shell PUA is in-between.

Effect of the type of the cationic sealing agents

The colors of the leathers and the coatings used in the last column from Table IX to XIII are white. The colors of the leathers and coatings in other columns are black. The sealing agents used in the preparation of finished black and white leathers are different. The black leather used aromatic cationic PU as a sealing agent and the white leather used the aliphatic cationic PU as a sealing agent. The two types of sealing agents did not show much influence to the wet rub resistance, solvent resistance, flex resistance, adhesive strength of the finished leather coatings.

In addition, the finished white leather using the interpenetrating PUA as a finishing system were exposed under UV light about 24 hours and compared with the corresponding finished leather which did not exposed under UV light, the white degree of the irradiated finished leather did not show a visible change and did not become yellow.

CONCLUSIONS

The synthesized anionic PU dispersion, the core-shell PUA and interpenetrating PUA composite emulsions all showed good film forming properties, good covering grain damage and mending properties, and strong adhesive force to the leather. The finished leathers were soft, flat, smooth, non-sticky and their grain patterns were clear. The interpenetrating PUA is better than the core-shell PUA, the core-shell PUA is better than the PU dispersion at wet rub fastness, solvent

resistance, adhesive resistance; however the PU dispersion and core-shell PUA both are better than the interpenetrating PUA at flex resistance by comparison.

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