Long-Chain Fatty Ammonium Quaternaries in Papermaking

Juha P. Koskela and Osmo E.O. Hormi*

University of Oulu, Department of Chemistry, Linnanmaa, FIN-90014 Oulu, Finland

ABSTRACT: A series of long-chain quaternary ammonium halogen esters (UKK-chemicals), quaternary dimethyl tallow epoxypropyl ammonium halogens (EPK1), quaternary ditallow methyl epoxypropyl ammonium halogens (EPK2), and EPK2 oligomers (EPK2P) were synthesized. At acidic, neutral, or slightly basic conditions, EPK1-, EPK2-, EPK2P-, and UKK-chemicals operate as cationic chemicals. They can be used, for example, as stock sizings, surface sizings, or fixatives. Stock sizing, surface sizing, and fixative experiments indicate that EPK1-, EPK2-, EPK2P-, and UKK-chemicals function at least as well as or better than the corresponding synthetic chemicals used in papermaking.

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Paper treatment chemicals can be placed into three different categories: hydrophobic sizing agents (i.e., internal and surface sizing agents), which reduce the natural tendency of fibers to interact with water and increase their hydrophobicity; dry-strength additives, which enhance the strength of individual fibers and the bonds between fibers; and wet-strength additives, which increase the wet strength of paper (1–3).

When an aqueous liquid contacts the surface of the paper, it must first wet the fibers, after which it tends to spread out along the fiber surfaces. Lateral movement on the surface of the paper (feathering) can be accelerated and enhanced by capillary action induced by closely parallel fibers lying on this surface (4,5). Liquid can also move transversely (penetrate) through the paper; it is drawn into the sheet structure by the capillary action of pores or spaces between the fibers.

All sizing agents must reduce fiber wettability, which is accomplished by the introduction of hydrophobic groups. Hydrophobicity is only one of the requirements necessary for effective sizing (6,7). In addition, the sizing agent must be well distributed over the fiber surfaces to ensure adequate water repellency throughout the paper structure, and sizing agent molecules must eventually be well anchored to the fiber surfaces.

A growing trend in the paper industry is the move toward a neutral pH sizing system whenever possible. One method for sizing paper internally at high pH involves the use of chemically reactive sizing agents. All cellulose-reactive sizings have a hydrophobic group attached to a cellulose-reactive functionality. The introduction in the last 55 yr of several synthetic sizing agents that react chemically with the hydroxyl groups of cellulose fibers marks a distinct departure from the traditional sizing process. The chemical reactivity of these amphipathic additives can produce, in principle, a permanently anchored monomolecular layer of hydrophobic material, which can provide excellent water repellency. The use of these agents has demonstrated their much greater sizing efficiency as compared to rosin sizing. Although more expensive than rosin, these materials are often superior on a cost–performance basis (8).

Various other types of sizing agents are often employed in the sizing process. These include rosin and wax emulsions and various polymeric dispersions in water (9,10). In the latter category, maleic anhydride copolymers with styrene have become especially popular as surface sizing agents (11). Aliphatic organic quaternary ammonium salts have been used to prevent penetration of all types of systems that contain an organic solvent, for example, to prevent penetration through the paper or board of a printing ink, coating composition, or lacquer dispersed into or dissolved in an organic solvent (12).

Although many synthetic organic molecules are capable of imparting water resistance to paper, only alkyl ketene dimer (AKD) (13) and alkyl succinic anhydride (ASA) (14) have been widely adopted by the paper industry. AKD is used more commonly in Europe (with 80–90% of the market), whereas in the United States the application of ASA is growing and today surpasses that of AKD.

This paper describes the reaction of long-chain FA with quaternary epoxypropyl ammonium halogens in the presence of catalysts and an appropriate solvent to afford long-chain quaternary ammonium esters (UKK-chemicals). Furthermore, we describe the reaction of long-chain dimethyl hydrogenated tallow alkyl amine and long-chain di-(hydrogenated tallow alkyl) methyl amine with epihalohydrins in the presence of catalysts and phase transfer catalysts to afford quaternary dimethyl tallow epoxypropyl ammonium halogens (EPK1) and quaternary ditallow methyl epoxypropyl ammonium halogens (EPK2). The preparation of EPK2 oligomers (EPK2P) is also reported. These cationic chemicals have been used as sizing chemicals, as internal sizing agents, and as surface sizing agents. Some of these chemicals have been used as fixative agents. The effects of the nature of Lewis acids (LA) and solvent also have been studied.

Some of the EPK-chemicals have been used in preparing protein hydrolyzate quaternary ammonium derivatives (15). According to the literature, all UKK-chemicals that include more than 20 carbons in the carbon chain are novel.

In the present case, all the reactions proceed conveniently and almost quantitatively under mild conditions. All products can be used as either aqueous solutions or dispersions with-

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*To whom correspondence should be addressed at University of Oulu, Department of Chemistry, Linnanmaa, P.O. Box 3000, FIN-90014 Oulu, Finland. E-mail: Osmo.Hormi@oulu.fi

out stabilizing agents. The reaction products were analyzed by using ^{1}H NMR, FTIR, and high-resolution MS.

EXPERIMENTAL PROCEDURES

Materials. Solvents were practical grade and used without further purification. Epichlorohydrin was a commercial 99% product. Epibromohydrin was a commercial 98% product. Long-chain hydrogenated dimethyl tallow amine was a commercial product from Akzo Nobel Surface Chemistry AB (Stockholm, Sweden). The chain-length distribution was 65% C_{18}, 30% C_{16}, and 5% C_{14}. Long-chain hydrogenated ditallow methyl amine was a commercial product from Akzo Nobel Surface Chemistry AB. The chain-length distribution was 65% C_{18}, 30% C_{16}, and 5% C_{14}. A mixture of FA composed of 60% palmitic and 40% stearic acid was obtained from Veitsiluoto Oy (Metsäkemian teollisuus, Oulu, Finland). Oleic acid was a commercial 70% product. Rosin acid (Veitsiluoto Oy) was a mixture of abietic acid (35%), dehydroabietic acid (20%), palustric acid (10%), isopimaric acid (7%), neoabietic acid (4%), and pimaric acid (3%). Glycidyl trimethyl ammonium chloride (GTMAC) was a commercial 95% (NMR) product (e.g., Raisio Chemicals Oy, Turku, Finland). Formaldehyde urea adduct was synthesized in our laboratory (University of Oulu, Finland) (16). Dimethylol melamine was a commercial product from Ciba Geigy (Basel, Switzerland). LP-wax acid was a commercial product from Clariant GmbH (Gersthofen site marketing waxes; Augsburg, Germany); the saturated chain-length distribution was C_{20} to C_{40}. AKD, ASA, and styrene maleic anhydride (SMA) were provided by Raisio Chemicals Oy.

Cobb 60 test. The most common aqueous absorption test is the Cobb test (17), which measures the amount of water absorbed by the sample during a certain time from an excess of water in units of g/m^2. This test is used to determine the degree of sizing, i.e., the water repellency of the paper.

^{1}H NMR. NMR spectra were recorded on a Bruker AM 200 (200.13 MHz) NMR spectrometer (Karlsruhe, Germany) using deuterated chloroform as solvent. Chemical shifts are reported in ppm (δ) with the corresponding scale calibrated to tetramethylsilane (TMS) as the internal reference or to the residual solvent signal. The following symbols were used in the multiplicity of resonances: *s* = singlet, *d* = doublet, *dd* = doublet of doublets, *t* = triplet, *q* = quartet, and *m* = multiplet.

FTIR. FTIR spectra were recorded on a Bruker IFS 66 FTIR spectrometer using chloroform as solvent.

Mass spectra. FAB-MS was carried out on a Kratos MS 80 FF spectrometer (Ramsey, NJ). Mass spectra were analyzed using the time-of-flight mode.

Gel permeation chromatography (GPC). The weight and average M.W. (M_w and M_n) of the oligomeric samples dissolved in THF were analyzed by a GPC system consisting of a Beckman 110B solvent delivery module pump (Fullerton, CA), Merck LaChrom refractive index detector (L-7490; Darmstadt, Germany), and Copam microcomputer (PC 386SXB/16; University of Oulu, Finland). PerkinElmer (Norwalk, CT) Brownlee columns (PE Plgel, 5 μm, Guard, 50 × 7.5 mm; and PE Plgel, 5 μm, 10^3, 300 × 7.5 mm) were used, at a flow rate of 1.0 mL/min. Samples were analyzed using a PicoLog program (Pico Technology Ltd., Cambridgeshire, United Kingdom), and an Microsoft Excel program was used to calculate the weight and average M.W. of the oligomer in relation to polystyrene standards.

The turbidity of the EPK and UKK aqueous solutions was recorded on an Elbecon Analite NTM 152 nephelometer (Arizona Chemical Oy, Oulu, Finland). Stock and surface sizing experiments were done in Stora Enso's pilot paper mill in Imatra, Finland.

Reaction of long-chain hydrogenated dimethyl tallow amine and long-chain hydrogenated ditallow methyl amine with epihalohydrins. Quaternary EPK1 and quaternary EPK2 were synthesized. Reaction conditions are shown in Table 1. The solvents were removed on a rotary evaporator under reduced pressure at room temperature. The product was isolated by recrystallization from ethyl acetate. The ratio between hydrogens (CH_2CH)O at 2.68–3.02 ppm and terminal –CH_3 at 0.78–0.92 ppm gave the epoxy content (Table 2).

Preparation of the quaternary EPK2 oligomers (EPK2P). A mixture of EPK2 (10 g, 15.9 mmol), 4-dimethylaminopyridine (0.3 g, 2.5 mmol), and toluene (15 mL) was stirred for 72 h at 100°C. The solvents were removed on a rotary evaporator under reduced pressure. Epoxide content was determined by ^{1}H NMR and showed that the epoxide content was decreased to about 20%. M_w and M_n of the product (EPK2P) were determined by GPC. M_w and M_n for the product were 1144 and 917, respectively.

Reaction of a mixture of FA, oleic acid, and LP-wax acid with GTMAC. Long-chain quaternary trimethyl ammonium chloride FA ester (TMACFE), long-chain quaternary trimethyl ammonium chloride oleic acid ester (TMACOE), and long-chain quaternary trimethyl ammonium chloride wax acid ester (TMACWE) were synthesized. Reaction conditions are shown in Table 1. An acid was dissolved in 2-propanol and was poured into a reaction vessel; the solution was heated in a 100°C oil bath while stirring; and GTMAC was added. Stirring was continued at the same temperature, after which the mixture was poured into a separation funnel and was allowed to cool to room temperature. The upper organic layer was separated and washed in succession with water. The final product was isolated by rotary evaporator under reduced pressure at room temperature. The purity of product was determined by ^{1}H NMR, FTIR, and MS. The ratio between hydrogens CH_2CO at 2.32–2.42 ppm and $–N^+(CH_3)_3$ at 3.35–3.5 ppm gave the ester content (Table 2). When LP-wax acid was used as a starting material, the final product, TMACWE, was isolated by recrystallization from methanol. The purity of product was determined by using FTIR (Table 2).

Reaction of a mixture of FA with glycidyl dodecyldimethylammonium bromide (GDDMAB) as well as with the quaternary EPK1. Long-chain quaternary dodecyldimethylammonium bromide FA ester (DDMABFE) and long-chain quaternary dimethyl tallow ammonium chloride FA ester (DMTACFE) were synthesized. Reaction conditions are shown in Table 1. Starting materials were stirred for 20 min at room temperature, after which the solution was heated in

TABLE 1
Preparation of EPK- and UKK Chemicals[a]

Chemical used in synthesis	Dosage of chemicals (g/mmol)	Reaction time	Reaction temperature	Isolation method	Analysis method	Product
Product 1						
DMTA +	20.0/67.3	10 min	Ambient	Recrystallization	^{1}H NMR	EPK1
EClH +	18.7/202.1			from	and	
KBr (anhydrous) +	1.72/14.5	+		ethyl acetate	MS	
$MgCl_2$ (anhydrous) +	0.5/5.3					
TBABr (anhydrous) +	0.34/1.1					
ethanol (94.0 vol%)	10 mL	4 h	55 (°C)			
Product 2						
DMTA +	43.0/144.7	30 min	Ambient	Recrystallization	^{1}H NMR	EPK1
chloroform +	30 mL	+		from		
EBH	26.5/193.7	7 d	72 (°C)	ethyl acetate		
Product 3						
DTMA +	15.0/28.0	20 min	Ambient	Recrystallization	^{1}H NMR	EPK2
EClH +	7.95/85.9			from	and	
KBr (anhydrous) +	1.29/10.8	+		ethyl acetate	MS	
$MgCl_2$ (anhydrous) +	0.38/4.0					
TBABr (anhydrous) +	0.26/0.8					
ethanol (94.0 vol%)	10 mL	4 h	55 (°C)			
Product 4						
DTMA +	10.2/19.0	6 h	Ambient	Recrystallization	^{1}H NMR	EPK2
acetonitrile +	15 mL	+		from	and	
EBH	5.5/40.2	21 h	60 (°C)	ethyl acetate	MS	
Product 5				Separation	^{1}H NMR,	
MFA +	50.0/186.9			funnel	FTIR,	TMACFE
2-propanol +	200 mL			+	and	
GTMAC	100.0/659.3	6 h	100 (°C)	rotary evaporator	MS	
Product 6				Separation	^{1}H NMR,	
Oleic acid +	100.0/405.1			funnel	FTIR,	TMACOE
2-propanol +	400 mL			+	and	
GTMAC	169.0/1115.5	12 h	100 (°C)	rotary evarator	MS	
Product 7						
LP-wax acid +	15.0/30.0			Recrystallization		
2-propanol +	100 mL			from	FTIR	TMACWE
GTMAC	13.6/89.9	16 h	100 (°C)	methanol		
Product 8						
MFA +	19.5/72.8	20 min	Ambient	Recrystallization		
GDDMAB +	33.8/96.3	+		from	FTIR	DDMABFE
$MgCl_2$ (anhydrous) +	0.5/5.3			ethyl acetate		
chloroform	20 mL	39 h	63 (°C)			
Product 9						
MFA +	9.0/33.6	20 min	Ambient	Recrystallization	^{1}H NMR	
EPK1 +	18.0/50.8	+		from	and	DMTACFE
$MgCl_2$ (anhydrous) +	0.24/2.5			ethyl acetate	FTIR	
2-propanol	20 mL	17 h	90 (°C)			
Product 10						
Rosin acid +	15.8/52.3			Recrystallization	FTIR	DMTACRE
2-propanol	45 mL			of impurities from		
EPK1	31.6/89.2	25 h	90 (°C)	ethyl acetate		

[a]Abbreviations: DDMABFE, quaternary dodecyldimethyl ammonium bromide FA ester; DMTA, dimethyl hydrogenated tallow alkyl amine; DMTACFE, quaternary dimethyl tallow ammonium chloride FA ester; DMTACRE, quaternary dimethyl tallow ammonium chloride rosin acid ester; DTMA, di (hydrogenated tallow alkyl) methyl amine; EBH, epibromohydrin; EClH, epichlorohydrin; EPK1, quaternary dimethyl tallow epoxypropyl ammonium halogens; EPK2, quaternary ditallow methyl epoxypropyl ammonium halogens; GDDMAB, glycidyl dodecyldimethylammonium bromide; GTMAC, glycidyl trimethyl ammonium chloride; LP-wax acid, very long chain (up to C40) carboxylic acid; MFA, mixture of FA; TBABr, tetrabutyl ammonium bromide; TMACFE, quaternary trimethyl ammonium chloride FA ester; TMACOE, quaternary trimethyl ammonium chloride oleic acid ester; TMACWE, quaternary trimethyl ammonium chloride wax acid ester; UKK, long-chain quaternary ammonium halogen esters.

an oil bath. Stirring was continued at the same temperature. The solvents were removed on a rotary evaporator under reduced pressure at room temperature. The final products were isolated by recrystallization from ethyl acetate. The purity of product was determined by using FTIR when GDDMAB was used as a starting material (Table 2). When EPK1 was used as a starting material, the purity of product was determined by ^{1}H NMR and FTIR. The ratio between hydrogens CH_2CO at 2.22–2.32 ppm and $–N^+(CH_3)_2(CH_2)–$ at 3.32–3.45 ppm gave the ester content (Table 2).

TABLE 2
Characterization of EPK1-, EPK2-, and UKK-Chemicals (i.e., TMACFE, TMACOE, TMACWE, DDMABFE, DMTACFE, and DMTACRE)[a]

Compound	Yield	Purity (%)	M.P. (°C)	HRMS	*m/z* (%)	FTIR acid/ester (cm^{-1})	^1H NMR (ppm)	Interpretation
EPK1	19.0 g, 72%	92	62–65	$C_{23}H_{48}NO$: (–HCl) calcd. 354.373, found	326 (38), 298 (35), 354 (100)	ND	0.78–0.92 (*t*, 3H), 1.05–1.45 (*s*, 34H), 2.68–2.82 (*q*, 1H), 2.88–3.02 (*t*, 1H), 3.30–3.70 (*m*, 10H)	Terminal –CH_3 Alkyl chain Epoxide ring Epoxide ring –CH_2–N–CH_2–$(CH_3)_2$
EPK2	11.7 g, 67%	82	65–70	$C_{40}H_{82}NO$: (–HCl) calcd. 592.640, found 592.637	564 (49), 527 (32), 592 (100)	ND	0.78–0.92 (*t*, 6H), 1.05–1.45 (*s*, 60H), 2.68–2.82 (*k*, 1H), 2.88–3.02 (*t*, 1H), 3.30–3.70 (*m*, 9H)	Terminal –CH_3 Alkyl chain –CH_2 Epoxide ring Epoxide ring –CH_2–N–$(CH_2)_2$–CH_3
TMACFE	74.0 g, 92%	83	58–64	$C_{24}H_{50}NO_3$: (–HCl) calcd. 400.379, found 400.371	354 (8), 400 (71), 372 (100)	1708.9/ 1737.3	0.82–1.00 (*t*, 3H), 1.20–1.50 (*s*, 34H), 2.32–2.42 (*t*, 2H), 3.35–3.50 (*s*, 9H), 3.60–3.75 (*d*, 2H), 4.20–4.32 (*m*, 2H)	Terminal –CH_3 Alkyl chain –CH_2–CO– –N–$(CH_3)_3$ –CH_2–N– –CH_2–O–
TMACOE	145.2 g, 90%	98	17–18	$C_{24}H_{48}NO_3$: (–HCl) calcd. 398.363, found 398.362	132 (23), 188 (19), 398 (100)	1695/ 1720.6	0.82–1.00 (*t*, 3H), 1.10–1.40 (*s*, 34H), 1.90–2.10 (*t*, 4H), 2.32–2.42 (*t*, 2H) 3.35–3.55 (*s*, 9H), 3.60–3.75 (*d*, 2H), 4.10–4.30 (*m*, 2H) 5.25–5.45 (*m*, 2H)	Terminal –CH_3 Alkyl chain –CH_2–CH=CH–CH_2– –CH_2–CO– –N–$(CH_3)_3$ –CH_2–N– –CH_2–O– –*CH*=*CH*–
TMACWE	15.6 g, 80%	80	95–101	ND	ND	1708.9/ 1737.3	ND	
DDMABFE	37.0 g, 85%	85	90–93	ND	ND	1708.9/ 1736.6	ND	
DMTACFE	19.0 g, 94%	85	115–119	ND	ND	1695.0/ 1720.6	0.78–0.90 (*t*, 3H), 1.10–1.40 (*s*, 68H), 2.22–2.32 (*t*, 2H), 3.32–3.45 (*s*, 8H), 3.45–3.60 (*d*, 2H), 4.18–4.30 (*m*, 2H)	Terminal –CH_3 Alkyl chain –CH_2 –CH_2–CO– –N–$(CH_3)_2$–CH_2 –CH_2–N– –CH_2–O–
DMTACRE	28.5 g, 83%	89	80–86	ND	ND	1707.3/ 1738.3	ND	ND

[a] High-resolution MS (HRMS) instrument: micromass, LCT; polarity, ES+; capillary (V), 3100.0; sample cone (V), 9.0; source temp. (°C), 100.0; desolvation temp. (°C), 120.0; Cl^- decomposed as HCl. In the case of the UKK, HRMS was calibrated to stearic acid derivative in the mixture of FA. ND, not determined due to long carbon chain. *s*, singlet; *d*, doublet; *dd*, doublet of doublets; *t*, triplet; *q*, quartet; and *m*, multiplet. For other abbreviations see Table 1.

Reaction of rosin acid with the quaternary EPK1. Long-chain quaternary dimethyl tallow ammonium chloride rosin acid ester (DMTACRE) was synthesized. Reaction conditions are shown in Table 1. Rosin acid was dissolved in 2-propanol and was poured into a reaction vessel. The solution was heated in a 90°C oil bath while stirring, then EPK 1 was added. Stirring was continued at the same temperature for 25 h. The final product was isolated by recrystallizing the impurities from ethyl acetate, after which the solvents were removed on a rotary evaporator under reduced pressure at room temperature. The purity of product was determined by FTIR (Table 2).

Internal sizing experiments with EPK2 and UKK-chemicals; experiments with EPK2, EPK2P, and DMTACFE as a surface sizing; and chemical bonding experiments with DMTACFE. A 5% aqueous dispersion of the EPK2 and 10% aqueous dispersions of the UKK-chemicals were tested in paper produced from various pulps. EPK2 and UKK-chemicals were mixed for 20 min with 50°C water to obtain a 1% solution just before the sizing test. Final concentrations of the EPK2 and UKK solutions were 1% before being added to the paper machine headbox.

Aqueous dispersions of EPK2, EPK2P, and DMTACFE were tested as surface sizing in paper produced from various

TABLE 3
Internal Sizing Experiments with EPK2- and UKK-Chemicals; Experiments with EPK2, the EPK2 Oligomer (EPK2P), and DMTACFE as Surface Sizings; and Chemical Bonding Experiments with DMTACFE[a]

Stock sizings used	Surface sizings used	Pulp (type)	Maturation temperature (°C)	Maturation period (min)	Dosage of surface sizing (g/m^2)/% of pulp	Cobb 60 tests before/after maturation
ASA	EPK2	30% pine, 70% birch, 20% PCC	125	5	0.121[b]	71.7/15.6
ASA	SMA	30% pine, 70% birch, 20% PCC	125	5	0.225[b]	17.7/17.0
AKD	EPK2	30% pine, 70% birch, 20% PCC	125	5	0.090[b]	20.7/17.5
AKD	SMA	30% pine, 70% birch, 20% PCC	125	5	0.146[b]	18.5/17.5
AKD	EPK2P	20% pine, 80% birch, 20% PCC	125	5	0.138[b]	—/21
AKD	SMA	20% pine, 80% birch, 20% PCC	125	5	0.138[b]	—/19.4
EPK2	EPK2	20% pine, 80% birch, 20% PCC	125	5	0.339[b]	48.6/20
EPK2	SMA	20% pine, 80% birch, 20% PCC-	125	5	0.276[b]	25.6/19.5
EPK2		100% chemical pine pulp	125	2.5	0.2[c]	135/20
EPK2		100% unbleached chemical pulp, 4% $CaCO_3$	125	5	0.15[c]	42/28
EPK2		20% pine, 80% birch, 20% PCC	125	5	0.15[c]	145/45
EPK2		Unbleached high-knotter pulp, 4% PCC	125	5	0.15[c]	50/29
TMACFE		100% chemical pine pulp	125	60	1.75[c]	111/25
TMACOE		100% chemical pine pulp	125	60	15[c]	125/105
DMTACFE		100% chemical pine pulp-	125	60	0.4[c]	110/20
DDMABFE		70% groundwood pulp, 30% pine pulp	125	60	0.3[c]	142/20
TMACWE		100% pine pulp, 2% $CaCO_3$	125	2.5	0.2[c]	118/48
DMTACFE		100% pine pulp, 10% $CaCO_3$	125	5	0.4[c]	112/18
DMTACFE		100% pine pulp, 20% PCC	110–115	2.5	0.4[c]	—/21
DMTACFE		70% groundwood pulp, 30% broke 2% $CaCO_3$	110–115	15	0.5[c]	—/20
DMTACFE		30% pine, 70% birch, 20% PCC	125	5	0.4[c]	109/19.4
ASA	DMTACFE	30% pine, 70% birch, 20% PCC	125	5	0.095[b]	72.2/17
ASA	SMA	30% pine, 70% birch, 20% PCC	125	5	0.225[b]	17.7/17
AKD	DMTACFE	30% pine, 70% birch, 20% PCC	125	5	0.094[b]	20.7/17.5
AKD	SMA	30% pine, 70% birch, 20% PCC	125	5	0.146[b]	18.5/17.5
DMTACFE	SMA	20% pine, 80% birch, 20% PCC	125	5	0.202[b]	—/72.5
AKD	DMTACFE	20% pine, 80% birch, 20% PCC	125	5	0.251[b]	—/61.1
ASA	SMA	20% pine, 80% birch, 20% PCC	125	5	0.179[b]	21.1/ 201
Formaldehyde urea adduct (reference)		100% chemical pine pulp	125	60	1.75[c]	112/94.8 ND[d]
Dimethylol melamine (reference)			125	60	1.75[c]	110/94.5 ND[d]
DMTACFE			125	60	1.75[c]	111.5/26.0 0[d]
DMTACFE + formaldehyde urea adduct			125	60	1.75[c]	97.3/20.6 6.7[d]
DMTACFE + dimethylol melamine			125	60	1.75[c]	93.6/21.6 8.2[d]

[a] PCC, precipitated calcium carbonate; dosage is calculated from dry fiber weight (w/w). ASA, alkenyl succinyl anhydride; SMA, styrene maleic anhydride; EPK2P, ditallow methyl epoxypropyl ammonium halogen oligomers; AKD, alkyl ketene dimer. For other abbreviations see Table 1.

[b] g/m^2.

[c] Percentage of dry fiber.

[d] Percentage chemically bonded to the fiber.

pulps. EPK2, EPK2P, and DMTACFE were first mixed with a 50°C starch solution for ~20 min. The final dry contents of EPK2, EPK2P, and DMTACFE were 5–6% of dry starch. Surface sizing was carried out with a size press by using a roll application. The reference used was a commercial SMA.

To determine the amount of DMTACFE that bonded chemically to the fiber, 1% aqueous solutions of the DMTACFE alone and together with a wet-strength sizing (formaldehyde urea adduct or dimethylol melamine) were tested in paper produced from 100% pine pulp. Wet-strength sizings were also used alone as reference chemicals. The results are shown in Table 3.

Use of EPK1, DMTACFE, and TMACWE as fixatives. A 1% aqueous solution of the EPK1 was tested as a fixative in coated broke with a 2.53% consistency. The change in turbidity of the filtrate was determined as a function of the chemical dosage, and obtained values were compared with values obtained by using the commercial fixative PAC (polyaluminum chloride). The results of the experiment are shown in the Table 4.

A 1% aqueous solution of the DMTACFE was tested as a fixative in coated broke with a 2.53% consistency. A 1.5% aqueous solution of the TMACWE was tested as a fixative in peroxide-bleached thermomechanical pulp (TMP) with a 3.8% consistency. The change in turbidity of the filtrate was determined as a function of the chemical dosage, and obtained values were compared with values obtained by using PAC. The results of the experiment are shown in the Table 4.

RESULTS AND DISCUSSION

Interest in the possibility of improving the substitution reaction between epichlorohydrin and long-chain hydrogenated dimethyl tallow alkyl amines or long-chain hydrogenated ditallow alkyl methyl amines as well as the usefulness of enhancing the esterification reaction between quaternary dodecyldimethyl epoxypropyl ammonium halogens or quaternary EPK1 and long-chain FA led us to investigate the use of a range of LA catalysts ($AlCl_3$, $FeCl_3$, KBr, and $MgCl_2$). In the case of EPK chemicals, we performed LA-catalyzed reactions at a molar ratio of 1.4–1.6:1:0.3 with GDDMAB or quaternary EPK1, long-chain FA, and catalyst. In the case of UKK-chemicals, we performed LA-catalyzed reactions at a molar ratio of 1.4–1.6:1:0.3 with GDDMAB or EPK1, long-chain FA, and catalyst. We observed that the nature of LA and solvent had dramatic effects on the product distribution obtained in these experiments.

In these experiments, when a mixture of long-chain hydrogenated dimethyl tallow alkyl amine and epihalohydrin or a mixture of long-chain hydrogenated ditallow alkyl methyl amine and epihalohydrin were stirred in the absence of solvents or catalyst, the desired epoxide product was not found in the reaction mixture. When epibromohydrin was used and the reaction was carried out using an appropriate solvent, the reaction took place and the EPK product was formed in nearly quantitative conversion. In contrast, when epichlorohydrin was used, the reaction gave unreacted starting materials and an unidentified product that contained less than 20% of the theoretical epoxide content.

TABLE 4
Use of EPK1, DMTACFE, and TMACWE as Fixatives

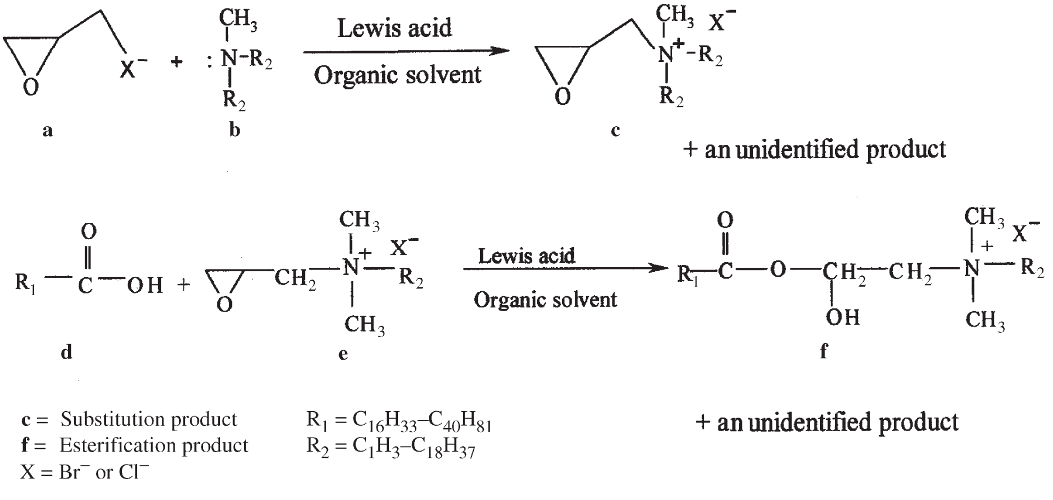
Chemical used	Chemical dosage (%)	Turbidity (NTU·10^3)	PAC[a] dosage (%)	Turbidity (NTU·10^3)
EPK 1	0.1	0.204	0.4	0.274
	0.3	0.147	0.8	0.260
	1.0	0.075	1.0	0.240
DMTACFE	0.1	0.204	0.4	0.274
	0.3	0.195	0.8	0.260
	1.0	0.140	1.0	0.240
TMACWE	0.05	0.196	0.3	0.200
	0.1	0.177	0.6	0.141
	0.3	0.172	1.0	0.073
	1.0	0.036	1.5	0.048

[a] PAC (polyaluminum chloride) was used as a reference chemical. For other abbreviations see Table 1.

Also, when a mixture of long-chain FA and quaternary epoxypropyl ammonium halogens was stirred in the absence of solvents or catalyst the desired ester product in the reaction mixture was not found. When quaternary trimethyl epoxypropyl ammonium halogens were used and the reaction was carried out using an appropriate solvent, the reaction took place and UKK products was formed in a nearly quantitative conversion. In contrast, when the quaternary dodecyldimethyl epoxypropyl ammonium halogens or quaternary EPK1 were used, the reaction gave unreacted starting materials and an unidentified product that contained less than 20% of the theoretical ester content.

Interest then focused on various LA and their ability to catalyze nucleophilic substitution reactions of the long-chain hydrogenated dimethyl tallow alkyl amine and also the long-chain hydrogenated ditallow alkyl methyl amine to the catalyst-activated epichlorohydrin as well as esterification reactions of long-chain FA to the catalyst-activated quaternary dodecyldimethyl epoxypropyl ammonium halogens or quaternary EPK1.

The products obtained are summarized in Scheme 1. The overall results are described in the text. As Scheme 1 shows,



SCHEME 1

when chemical **(b)** was used as a starting material, the reaction gave either a substitution product **(c)**, unreacted starting materials, or the unidentified product, which had <20% of the desired epoxide content, depending on the LA and the solvent used.

The reaction activated by anhydrous $MgCl_2$, which is a bidentate LA and is able to form chelates with Lewis bases with two empty *p*-type orbitals of the metal, in chloroform gave only unreacted starting materials and also an unidentified product that had less than 20% of the desired epoxide content. In acetonitrile, the final reaction mixture contained the desired product **(c)** with 75% epoxide content, but only in 25% yield; the residue consisted of the starting materials and heretofore unidentified by-products.

Because the reactions to obtain substitution products from epichlorohydrin using tertiary amines with $MgCl_2$ as catalyst in aprotic solvents were not as successful as desired, our next attempt was to carry out the reactions in protic solvents such as ethanol (94.0 vol%). We also used tetrabutyl ammonium bromide as a phase transfer catalyst, which is known to enhance nucleophilic substitution processes. When $MgCl_2$ was used together with ethanol and the phase transfer catalyst, the final reaction mixture contained the product **(c)** with 65% epoxide content, but only in 40% yield; the residue contained the starting materials and heretofore unidentified by-products.

Having failed to obtain good yields of the desired substitution product **(c)** with the above-mentioned methods, we finally tested mixed catalysts (anhydrous $MgCl_2$ and KBr) with the phase transfer catalyst in ethanol (94.0 vol%). We reasoned that this combination of catalysts would generate a stronger LA ($MgBr_2$) *in situ*. The stronger LA would then have a greater ability to activate the epoxide toward nucleophiles. Mixed catalysts with the phase transfer catalyst were ideal for our synthesis.

As shown in Scheme 1, when chemical **(e)** was used as a starting material, the reaction gave either esterification product **(f)**, unreacted starting materials, or the unidentified product, which had less than 10% of the desired ester content, depending on the LA and the solvent used.

We began this experimentation with a commonly used strong LA, $AlCl_3$, which is a typical monodentate catalyst. With the reaction activated by $AlCl_3$ in chloroform, the final reaction mixture contained 20% of the esterification product **(f)**. In dichloromethane, the final reaction mixture contained the desired product **(f)** with 60% ester content, but only in 30% yield; the residue consisted of the starting materials and unidentified by-products. We reasoned that the modest reactivity enhancement of $AlCl_3$ limited the esterification reaction between GDDMAB or quaternary EPK1 and long-chain FA.

Because the above-mentioned methods did not give the desired esterification product **(f)**, we tested another catalyst, anhydrous $FeCl_3$, in chloroform when GDDMAB was used and in 2-propanol when EPK1 was used. The reaction gave the desired product **(f)**, with ~90% ester content and in 85–94% yields. Surprisingly, the color of the final product was red. When using these chemicals as internal sizing agents or surface sizing agents, they must be colorless.

Our next attempt was to carry out the reactions using $MgCl_2$ as catalyst. The reaction was activated by anhydrous $MgCl_2$, a bidentate LA that is able to form a chelate with Lewis bases with two empty *p*-type orbitals of the metal, in chloroform when GDDMAB was used and in 2-propanol when EPK1. The $MgCl_2$ finally gave good yields and purity (based on ester content) of the desired esterification product **(f)**, as shown in Table 2.

As explained above, the choice of LA and solvent proved crucial to the success of the substitution and esterification reactions. These reactions also can be successfully accomplished on a larger-scale synthesis.

Previous reports indicated that a temperature rise increases quaternary ammonium salt adsorption on cellulose (18). The temperature used in our present work was the same in all the experiments because the purpose was to simulate the conditions used in the paper industry.

The prolonged maturation period greatly affects the development of sizing using EPK- and UKK-chemicals. For example, when quaternary EPK2 was used as the stock sizing in paper that contained 20% pine, 80% birch pulp, and 20% precipitated calcium carbonate (PCC), the Cobb 60 instant number obtained was 145 and the Cobb oven number (125°C/5 min for each experiment) obtained was 45 (Table 3). When ASA was used as the stock sizing and EPK2 was used as the surface sizing in paper that contained 30% pine, 70% birch, and 20% PCC, the Cobb 60 instant number obtained was 71.7 and the Cobb 60 oven number obtained was 15.6 (Table 3).

When long-chain quaternary DMTACFE was used as the internal sizing in paper that contained 100% pine pulp and 10% $CaCO_3$, the Cobb 60 instant number obtained was 112 and the Cobb oven number obtained was 18 (Table 3). When ASA was used as the internal sizing and DMTACFE was used as the surface sizing in paper that contained 30% pine, 70% birch, and 20% precipitated calcium carbonate (PCC), the Cobb 60 instant number obtained was 72.2 and the Cobb 60 oven number obtained was 17.0 (Table 3).

The softening temperature of EPK- and UKK-chemicals was low enough (17–115°C) to provide moderate mobility during the maturation of sized paper at 125°C, causing the material to flow and spread over fiber surfaces. Most importantly, the temporarily enhanced mobility during the elevated maturation period encouraged polar groups to reorient inward from the air–particle interface, thus creating a strongly hydrophobic surface. Once the paper matured, these reoriented polar groups remained fixed at room temperature because of their lower mobility in the solid state.

The origin and processing of the fiber frequently affects sizing development. A rough correlation exists between pulp sizability and pulp impurities content. For instance TMP and bleached pulps with high PCC content are difficult to size. In contrast, unbleached pulps generally have high carboxyl content, are quite easy to size, and often show a self-sizing tendency because of their natural resin content (19).

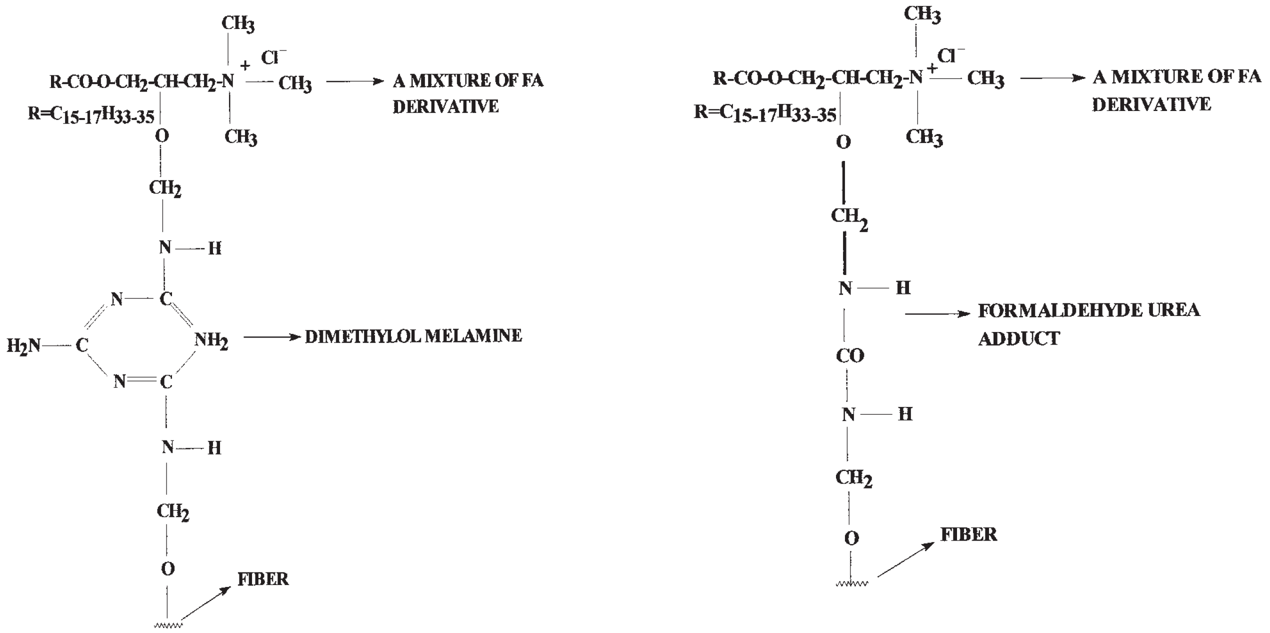
For example, Table 3 shows that when EPK2 was tested as a stock sizing in paper that contained 20% pine pulp, 80% birch pulp, and 20% PCC, the Cobb 60 instant number was 145 and the Cobb oven number was 45. When EPK2 was tested as a stock sizing in paper that contained unbleached high-knotter pulp with 4% PCC, the Cobb 60 instant number was 50 and the Cobb 60 oven number was 29. The data discussed in this section clearly show that the elevated maturation period greatly affected the development of sizing when using EPK chemicals.

As shown in Table 3, when DMTACFE was tested as an internal sizing in paper that contained 30% pine pulp, 70% birch pulp, and 20% PCC, the Cobb 60 instant number was 109 and the Cobb oven number was 19.4. When long-chain quaternary DDMABFE was tested as an internal sizing in paper that contained 70% groundwood pulp and 30% pine pulp with 2% $CaCO_3$, the Cobb 60 instant number was 142 and the Cobb 60 oven number was 20. As discussed in this section, the data clearly show that the elevated maturation period greatly affected the development of sizing when using EPK and UKK chemicals.

One of the drawbacks of UKK sizing is the rather slow curing process. This is particularly troublesome in fine papermaking because the paper is also surface-sized on the machine. It is often desirable for some sizing to take place before size pressing to obtain the best operability of the machine. This problem can be overcome in three different ways: (i) One way is to decrease the speed of the machine. This will increase the time the web remains at high temperature before moving to the size press, and the sheet can be overdried to a residual moisture below the 5–7% equilibrium moisture. Both measures promote the rate of sizing development. However, the main disadvantage with this approach is the loss in production. (ii) A second way to increase sizing before size pressing is to increase the size dosage. In this way sizing may be increased to a sufficient level since enough UKK molecules may adsorb with the fiber giving the desired water resistance. However, this approach adds to the cost. (iii) The third solution is to use a UKK sizing formulation containing a promoter agent (Table 3). Ideally, the promoter agent is incorporated into the sizing formulation to give the desired intimate contact between the UKK sizing agent and the promoter during the reaction with the fiber. The proposed reactions between UKK-chemicals and the fiber when using promoter agents are summarized in Scheme 2.

The mechanism of the TMACFE–cellulose interaction may be unequivocally demonstrated by measuring TMACFE–cellulose stability in a water-soluble solvent of TMACFE, such as boiling MeOH. This is illustrated in Figure 1. The ability of water to dissolve TMACFE from cellulose is limited. Under these circumstances, coulombic attraction between the positive heads and the negative charges on the surface is strong enough to keep the TMACFE at the fiber surface. When efficiency of the nonpolar solvent increases, the solvent thoroughly solubilizes the TMACFE ($\varepsilon_{water} = 78.5$, $\varepsilon_{MeOH} = 32.7$) (20).

In order to determine the amount bonded chemically to the fiber of the size TMACFE, sizing was performed on a suitable number of sheets. The sheets were weighed while dry, after which they were leached overnight with boiling methanol. After this treatment, the amount of sizing remaining chemically bonded to the sheets was calculated according to the following equation: weight of sheets before the leach – mass of matter detached in the leach = amount of chemically bonded sizing. The material detached from unsized sheets has been taken into account in the calculations. Table 3 clearly shows that when TMACFE is chemically bonded to fiber (Scheme 2), the covalent bond between the TMACFE and fiber is much stronger than the electrostatic interaction between the fiber and TMACFE. It is therefore impossible to solubilize the TMACFE when extracting with MeOH.



SCHEME 2

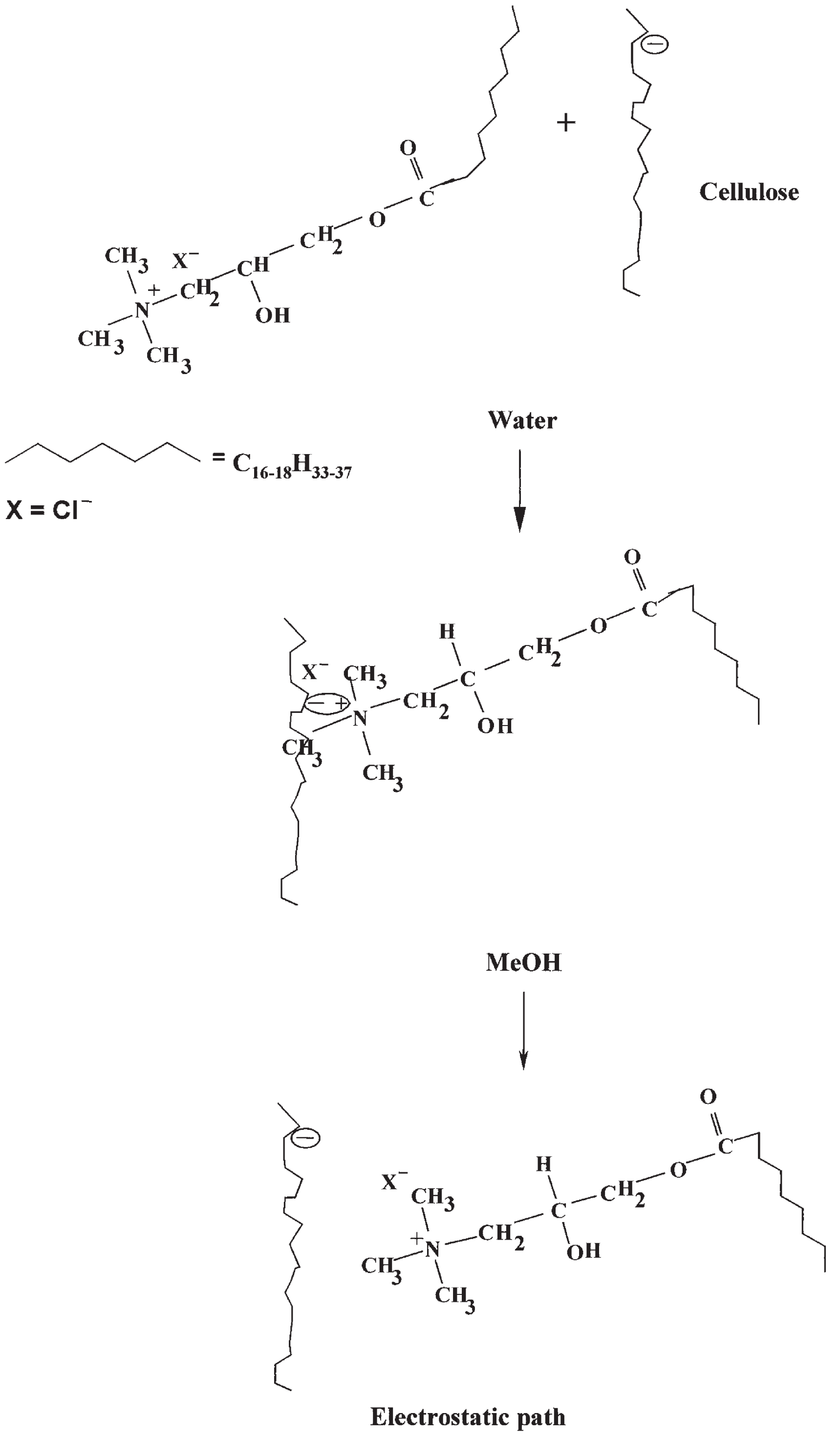


FIG. 1. Demonstration of the nature of TMACFE–cellulose interaction. MeOH, methanol; TMACFE, quaternary trimethyl ammonium chloride FA ester.

In addition, Table 3 shows the effect of promoter agents. When 1% aqueous solutions of the DMTACFE were tested as internal sizings in paper produced from 100% pine pulp, the Cobb 60 instant number was 111.5, and the Cobb oven number was 26. When DMTACFE was used together with a formaldehyde urea adduct, the Cobb 60 values were 97.3 and 20.6, respectively. When DMTACFE was used together with dimethylol melamine, the Cobb 60 values were 93.6 and 21.6, respectively.

One percent aqueous solutions of the quaternaries EPK1 and DMTACFE were tested as fixatives in coated broke with a 2.53% consistency, and a 1.5% aqueous solution of the long-chain quaternary TMACWE was tested as a fixative in peroxide-bleached TMP with a 3.8% consistency. The obtained values were compared with values obtained by using PAC. For example, Table 4 shows that when EPK 1 was tested as a fixative with a 1.0% dosage, turbidity of the filtrate was 0.075 nephelometric turbidity units (NTU)$\cdot 10^3$. When PAC was used at the same dosage, the turbidity of the filtrate was 0.240 NTU$\cdot 10^3$. When DMTACFE was tested as a fixative with a 1.0% dosage, turbidity of the filtrate was 0.140 NTU$\cdot 10^3$. When PAC was used with the same dosage, turbidity of the filtrate was 0.240 NTU$\cdot 10^3$. The data discussed here clearly show that some of the EPK- and UKK-chemicals are also very functional as fixatives.

Known sizing chemicals usually have one or more of the following drawbacks: (i) They are not water-soluble and require stabilizers when being dispersed in water. (ii) They are not adsorbed on the fiber surface as effectively as needed from dilute aqueous solutions. (iii) In an aqueous solution, for instance, AKD and ASA hydrolyzed rapidly to unusable sizing chemicals. (iv) The product of the hydrolysis of ASA has been shown to inhibit sizing (21–23). (v) They do not work effectively in the presence of filler, and their manufacture is difficult.

EPK- and UKK-chemicals can be used as aqueous solutions or dispersions without the need for stabilizing agents. Compared to reactive sizing chemicals such as ASA or AKD, they are very stable. For example, EPK2 epoxide content after 1 mon was still about 50%, and DMTACFE ester content after 1 yr was still about 78%. Also, all the reactions proceed conveniently and with almost quantitative results under mild conditions.

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REFERENCES

1. Hormi, O.E.O., and J.P. Koskela, A Papermaking Process Containing Tri- or Tetraalkylammonium Cationic Chemical, European Patent EP 918104 A1 19990526 (1999).
2. Hormi, O.E.O., and J.P. Koskela, Menetelmä paperin valmistamiseksi ja kationinen kemikaali, Förfarande för framställning av papper och en katjonisk kemikalie, Finnish Patent 103353 (1999).
3. Roberts, J.C., Chemical Additives in the Paper Formation Process and The Surface Modification of Paper, in *The Chemistry of Paper*, The Royal Society of Chemistry, London, 1996, Chapters 7 and 8.
4. Ross, S., and I.D. Morrison, Capillarity of Pure Liquids, in *Colloidal Systems and Interfaces*, John Wiley & Sons, New York, 1988, Chapter II.A, pp. 69–125.
5. Hiemenz, P.C., Surface Tension and Contact Angle, in *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1986, Chapter 6, pp. 287–352.
6. Contact Angle of Water on Paper and Paperboard, Scandinavian Pulp Paper and Board Testing Committee, Stockholm, Sweden, 1966, SCAN Method P-18:66.
7. Davison, R.W., The Sizing of Paper, *TAPPI 58*:48–57 (1975).
8. Roberts, J.C., Neutral and Alkaline Sizing, in *Paper Chemistry*, Chapman & Hall, Glasgow, 1996, Chapter 9, pp. 140–160.
9. Porter, R.B., and J.M. Behnke, Internal Sizing with Wax Sizes, *TAPPI 42*:140A–142A (1959).
10. Berrong, H., and R. Terch, New Application for Wax Emulsions in Paper Sizing Emphasizes Savings, *Paper Trade J. 151*:46–48 (1967).
11. Christman, R.J., Neutral Sizings Are Proving Their Worth in Mill Applications, *Ibid. 151*:38–39 (1967).
12. Dessauer, G., and H. Berenbold, Agent for Improving the Printability of Paper and Board, U.S. Patent 4,857,110 (1987).
13. Davis, J.W., W.H. Robertson, and C.A. Weisgerber, A New Sizing Agent for Paper—Alkylketene Dimers, *TAPPI 39*:21–23 (1956).
14. Wurzburg, O.B., Process of Sizing Paper with a Reaction Product of Maleic Anhydride and an Internal Olefin (for National Starch), U.S. Patent 3,821,069 (1974).
15. Hasegawa, M., Cosmetics Containing Protein Hydrolyzate Quaternary Ammonium Derivatives, Jpn. Patent 3,089,602 (2000).
16. Springer, J., *Beilstein's Handbuch der Organischen Chemie*, Deutschen Chemischen Gesellschaft, Berlin, 1921, Vol. 3, p. 59.
17. TAPPI T 441 om-90, Water Absorptiveness of Sized (non-bibulou) Paper and Paperboard (Cobb test), TAPPI Press, Norcross, GA, 1996.
18. Puchta, R., Cationic Surfactants in Laundry Detergents and Laundry Aftertreatment Aids, *J. Am. Oil Chem. Soc. 61*: 367–376 (1984).
19. Swanson, J.W., and S. Cordingly, Surface Chemical on Pitch II. The Mechanism of Self-Sizing in Papers Made from Wood Pulps, *TAPPI 42*:812–812 (1959).
20. Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, 2nd edn., Longman, London, 1986, p. 390.
21. Roberts J.C., and W.R. Wan Daud, *Proceedings of the 10th Cellulose Conference*, University of Manchester Institute of Science and Technology, Department of Paper Science, Manchester, England.
22. McCarthy, W.R., and R.A. Stratton, Effects of Drying on ASA Esterification and Sizing, *TAPPI 70*:117–121 (1987).
23. Roberts J.C., and W.R. Wan Daud, Wood Processing and Utilisation, in *Proceedings of the Cellulcon Japan Conference,* edited by J.F. Kennedy, G.O. Phillips, and P. Williams, Ellis Horwood, Chichester, United Kingdom, 1989, pp. 133–142.

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