TABLE III. PREPARATION OF BUTYL LACTATE FROM AMMONIUM LACTATE RECYCLING EXPERIMENTS

Cycle	Ammonium Lactate Moles	Temperature, ° C.		Time, Hours	Ester, Moles	NH_3, Moles
		Reaction[a]	Vapor[b]			
Series A						
1	1.00	104–134	115	5.5	0.58	0.75
2	1.00	105–139	115	5.5	0.82	0.79
3	1.00	109–146	114	3.5	0.77	0.75
4	1.00	112–150	115	4.0	0.93	0.86
5	1.00	112–149	115	4.0	0.82	0.72
6	1.00	112–157	114	4.0	0.91	0.79
7	1.00	112–151	114	3.5	0.86	0.71
8	1.00	113–157	114	4.0	0.88	0.74
9	1.00	113–152	112	4.0	0.90	0.76
Total	9.00				7.47	6.87
Over-all yield: butyl lactate, 83%; NH_3, 75%.						
Series B						
1	1.00	104–136	115	6.5	0.64	0.85
2	0.64	108–172	115	3.5	0.49	0.55
3	0.49	108–140	115	4.0	0.50	0.48
4	0.50	108–144	114	6.5	0.54	0.46
5	0.54	107–140	115	5.5	0.53	0.53
6	0.53	108–155	113	4.0	0.46	0.46
7	0.46	108–159	113	2.5	0.36	0.37
Total	4.16				3.52	3.70

Over-all yield after seven cycles: butyl lactate, 85%; NH_3, 89%.

[a] Initial and final temperature of reaction mixture.
[b] Final temperature of refluxing vapor.

Catalysis Study. Because the reaction of ammonium lactate with butanol bears some resemblance to esterification, an attempt was made to accelerate this reaction with catalysts. Hence the reaction of ammonium lactate with butanol was conducted in the presence of 5 to 10 mole % of various salts and other reagents. Ammonium sulfate, ammonium *p*-toluenesulfonate, sodium acetate, and aluminum chloride did not show any catalytic activity. Boric acid, trihexylamine, basic aluminum acetate, and silica gel exerted some catalytic activity, reducing the time of reaction by approximately one half. Carrying out the reaction under an efficient column also reduced the reaction time (Expt. 3, Table I). The conversion to butyl lactate was not greatly affected by these various agents.

PREPARATION OF BUTYL LACTATE FROM AMMONIUM LACTATE—RECYCLING OF BY-PRODUCTS

The data in Table I show that the reaction of ammonium lactate with butanol results in approximately 50 to 60% conversion of the salt to butyl lactate. Because the probable by-products of this reaction are essentially esters of polylactic acid, it seemed likely that recycling the by-products would materially increase the yield. To obtain an estimate of the ultimate yield of butyl lactate from the reaction of ammonium lactate with butanol, a series of batch reactions was carried out in which the by-products (the distillation residues) were recycled. The reaction mixture after cycle 1 was composed of 1 mole of fresh ammonium lactate, 2.5 moles of fresh butanol and distillation residue (from the isolation of butyl lactate from the previous cycle). The reactions were conducted as described under "Experimental Procedure." The over-all yield was 7.47 moles of butyl lactate from 9.00 moles of ammonium lactate or 83% (Table III, series A). The, yield of ammonia, expected to be better than 85% from the data of Table I, was only 75% for some undetermined reason (perhaps the butanol fraction, which was not recycled, contained ammonia).

A similar series of recycling experiments was conducted in which the recovered butanol as well as by-products was used in the next cycle (Table III, series B). The reaction mixture, after the first cycle, comprised recovered butanol and distillation residue from the preceding cycle and fresh ammonium lactate and butanol (equivalent to the butyl lactate isolated in the previous cycle). In this instance the yield of both butyl lactate and ammonia was highly satisfactory—85 and 89%, respectively.

Presumably, in the reaction of ammonium lactate with other alcohols the yield of lactic ester would be high if the by-products of the reaction were recycled.

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Plasticizers from Lactic Esters and Dibasic Acids

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INTEREST in the utilization of lactic acid in the manufacture of plasticizers has been intensified in recent years by published data showing that lactic acid can be produced at a cost competitive with currently used plasticizer intermediates (*3*) and that highly efficient plasticizers can be made from lactic acid (*7, 8*). Recurrent shortages and threats of shortages of key intermediates currently used in plasticizer manufacture have stimulated interest in the use of lactic acid as an extender for scarce materials. Since lactic acid is both an acid and an alcohol, it can be used as an extender of either the acidic or the alcoholic component of conventional ester type plasticizers.

Previous papers in this series reported on the suitability as plasticizers of esters of lactic acid acylated with alkyl chloroformates (*8*) and diethylene glycol bischloroformate (*7*). This paper describes similar esters of adipic, phthalic, maleic, succinic, sebacic, carbonic, and benzenephosphonic acids. These esters have the type formula $X[COOCH(CH_3)COOR]_2$ where $X(COOH)_2$ is the dibasic acid used and $CH_3CHOHCOOR$ is the lactate used to make the compound. Most attention was devoted to the adipic and phthalic esters because these acids are available at low cost and are widely used in the plasticizer industry.

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Table I. Properties of Lactate Esters Esterified with Dibasic Acids

Ester		Boiling Points, ° C.						Properties of Plasticized Polyvinyl Chloride[a]					Compatibility with Cellulose Acetate[c]
Lactate used	Dibasic acid used	0.01 mm.	0.1 mm.	1.0 mm.	10 mm.	d_4^{20}	Viscosity, 20°, Cp.	Compatibility[b]	Tensile strength, lb./sq. inch	Elongation, %	Modulus (100%), lb./sq. inch	Brittle point, ° C.	
Ethyl	Adipic	100	130	168	214	1.1075	49.6	CB	3420	350	1370	−28	C
Propyl		105	136	174	221	1.0865	61.5	CB	3480	340	1370	−24	C
Butyl		122	155	194	240	1.0543	41.4	C	3060	330	1170	−30	C
Isobutyl		118	149	188	235	1.0479	53.3	C	3390	340	1340	−16	C
sec-Butyl		106	138	177	244	1.0574	75.6	CB	3330	330	1580	−20	C
2-Ethylhexyl		160	193	233	280	0.9997	68.0	C	3020	260	1255	−44	I
n-Octyl		167	202	243	292	0.9960	53.7	C	3070	360	1270	−40	I
2-Octyl		156	188	227	272	0.9929	82.4	C	3010	280	1170	−31	I
3,5,5-Trimethylhexyl		164	199	239	288	0.9881	117.0	C	3150	325	1470	−22	I
Allyl		111	144	185	232	1.1085	42.0	CB	3030	300	1140	−37	C
2-Butoxyethyl		159	192	233	282	1.0668	71.9	CB	3230	300	1230	−38	C
2-Hexyloxyethyl		178	213	255	...	1.0327	66.5	CB	3100	370	1180	−41	I
2-(2-Butoxyethoxy) ethyl		189	224	268	...	1.0725	79.2	CB	3080	280	1230	−35	C
Tetrahydrofurfuryl		166	200	240	288	1.1677	526	CB	3520	370	1270	−11	I
1-Carbethoxyethyl		155	188	227	275	1.1478	544	CB	3680	310	2230	−7	C
1-Carbobutoxyethyl		171	208	247	297	1.1026	284	CB	3580	270	1910	−13	C
Methyl[d]	Phthalic	113	145	186	235	1.2242	7495	C	3570	220	2500	9	C
Ethyl[e]		118	150	190	239	1.1715	934	C	3780	290	2560	9	C
Butyl		135	169	208	256	1.1094	283	C	3580	310	1800	1	C
2-Ethylbutyl		152	187	228	278	1.0878	882	C	3700[f]	340[f]	2240[f]	−2[f]	CI
n-Octyl		176	212	254	...	1.0381	250	C	4500	320	2300	−11	I
2-Ethylhexyl		166	203	245	298	1.0423	474	C	3560[f]	350[f]	1910[f]	−6[f]	I
2-Ethoxyethyl		157	191	234	284	1.1622	725	I	3370	310	2020	−2	C
2-Butoxyethyl		173	209	251	...	1.1092	338	CB	3640	280	2110	−8	C
2-(2-Butoxyethoxy)ethyl		200	218	282	...	1.1130	298	CB	3820	310	2010	−14	C
Allyl		128	162	203	257	1.1693	351	C	3740	255	2780	−4	C
Tetrahydrofurfuryl		182	220	265	...	1.2188	2009	C	3610	240	3060	19	C
Ethyl	Sebacic	128	160	199	244	1.0549	58.3	CB	3130	340	1290	−28	C
Butyl		148	182	222	270	1.0200	48.7	C	2970	350	1190	−31	CI
n-Octyl		186	223	266	...	0.9782	63.0	C	3080	340	1360	−40	I
2-Octyl		172	208	249	...	0.9740	90.9	C	2920	350	1230	−38	I
Methyl	Succinic	80	110	146	190	1.1925	140.6	I	3300	220	2550	..	C
Ethyl		87	117	153	198	1.1344	54.0	C	3760	250	2080	−8	C
Butyl		107	139	178	227	1.0714	44.7	C	3310	310	1410	−21	C
n-Octyl		158	191	231	281	1.0042	56.8	C	3070	320	1440	−29	I
Allyl		98	129	167	214	1.1353	48.9	I	2860	370	1230	−23	C
Ethyl	Maleic	60	89	124	170	1.1244	22.9	I	3590[f]	310[f]	2230[f]	−7[f]	C
Butyl		105	136	174	221	1.0852	74.3	C	>3240	>330	1670	−19	C
Isobutyl		97	127	166	212	1.0847	189.5	C	3130	365	1620	−12	C
2-Ethylhexyl		150	(0.03 mm.)	...	...	1.0134	110.4	C	3450[f]	340[f]	1610[f]	−36[f]	I
Allyl		100	131	169	215	1.1562	.....	I	3530	340	2140	−22	C
Butyl	Benzene-phosphonic	130	(0.02 mm.)	...	...	1.1082	52.7	CB	3130	350	1490	−11	C
Allyl	Carbonic	72	101	135	178	1.1284	26.3	I	3800	310	2270	−11	CI
Di-2-ethylhexyl phthalate (Control)		120	153	192	240		84	C	3070	290	1500	−32	I

[a] A 95:5 copolymer of vinyl chloride and vinyl acetate containing 35% plasticizer.
[b] C = Compatible; I = incompatible; CI = borderline; B = compatible when milled but bled on aging.
[c] High acetyl cellulose acetate containing 20% plasticizer.
[d] Melting point, 50–55° C.; n_D and d on supercooled liquid.
[e] Melting point, 55–60° C.; n_D and d on supercooled liquid.
[f] Properties determined with undistilled material.

PREPARATION AND PROPERTIES OF ESTERS

Table I shows the esters studied and the properties determined. Additional data on the preparation and properties of these esters have been published elsewhere (*5*, *6*).

The boiling points shown in Table I were read from the Cox charts previously published (*5*, *6*). Most of the esters had boiling points higher than that of di-2-ethylhexyl phthalate. Comparison of the vapor pressure curves of the esters in Table I with those of the corresponding esters not containing lactate radicals—for example, bis(butyl lactate), adipate with dibutyl adipate—shows that the vapor pressure of the esters containing lactate radicals is only 3 to 5% of that of the corresponding simple esters. Additional data on densities and viscosities are given in references (*5*) and (*6*).

Evaluation as Plasticizers. Most attention was devoted to polyvinyl chloride because this resin accounts for the largest volume of plasticizers, and its use is still expanding. The compounding and testing procedures have been described previously (*7*), and the results are summarized in Table I. As judged by modulus and brittle point, about one fourth of the esters are more efficient plasticizers for the 95% vinyl chloride copolymer than is di-2-ethylhexyl phthalate. Nearly all milled well and appeared compatible when tested, but several samples showed "bleeding" or spewing after being kept several months. Possibly some of these, which otherwise appear attractive as plasticizers, could be used in blends, thus improving their limited compatibility.

The presence of rings in the molecular structure of the esters markedly raised the brittle points of the plasticized vinyl resin, as is illustrated by the tetrahydrofurfuryl and the phthalate esters. A similar effect is produced by lactyllactate radicals, as in ethyl and butyl lactyllactate adipates—1-carbethoxyethyl and 1-carbobutoxyethyl, lactate adipate, respectively. The esters that appear to be of most interest as plasticizers for vinyl resin are the adipates and sebacates of the butyl and the octyl lactates. They combine good compatibility with high efficiency and exceptional permanence.

Compatibility of the esters with high acetyl cellulose acetate was determined by casting plasticized films from solution in acetone. As may be seen in Table I, most of the esters were compatible at 20% concentration. In many instances the presence of the lactate radicals in the plasticizers has greatly improved the compatibility with cellulose acetate. At the same time, of course, volatility is much reduced, thus providing a unique group of very high boiling compatible plasticizers for cellulose acetate.

DIRECT ESTERIFICATION OF ALKYL LACTATES WITH DICARBOXYLIC ACIDS

In the preparation of small amounts of these compounds (listed in Table I) for screening purposes the dibasic acid chlorides were used in most cases as a matter of convenience (*5*, *6*). This method was obviously impractical for commercial production of the compounds, and so a study was made of the reaction of dicarboxylic acids with alkyl lactates.

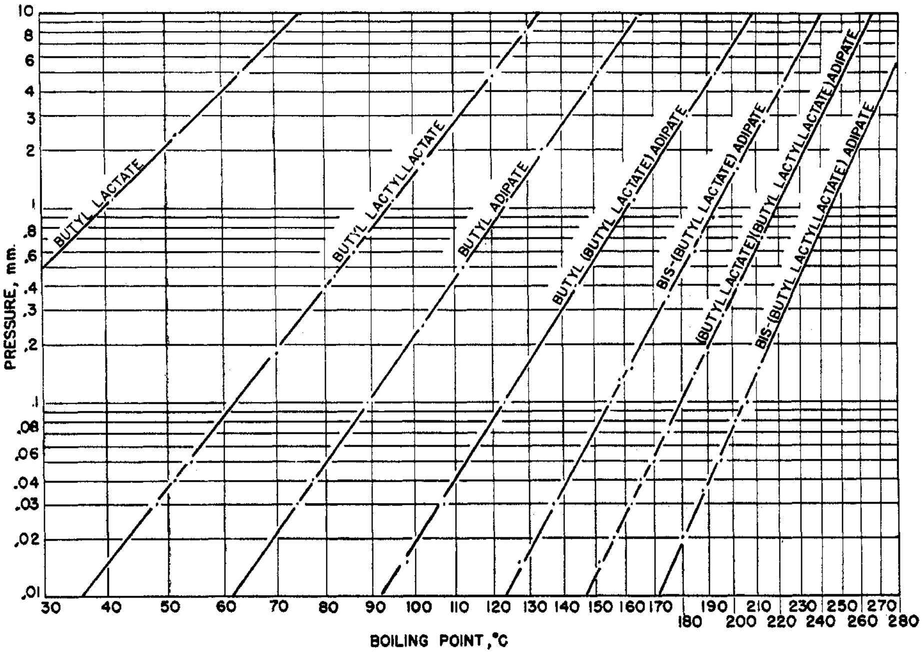


Figure 1. Relationship of Boiling Points to Pressure for Various Esters

On the basis of desirability, cost, ease of preparation, and availability of intermediates, butyl lactate adipate appeared the most attractive of the diesters screened. Hence, in the present work, most attention was devoted to the esterification of butyl lactate with adipic acid. A few experiments were run in which butyl or capryl lactate was esterified with sebacic, maleic, or phthalic acid or anhydride.

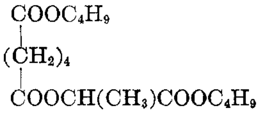
Since a lactate ester is also an alcohol, it is capable of undergoing self-alcoholysis when heated in the presence of strong acidic or basic catalysts (*1*). This results in the formation of linear polyesters:

$$2\mathrm{CH_3CHOHCOOR} \longrightarrow \mathrm{CH_3CHOHCOOCH(CH_3)COOR} + \mathrm{ROH}$$

$$n\mathrm{CH_3CHOHCOOR} \longrightarrow \mathrm{HO[CH(CH_3)COO]}_n - \mathrm{R} + (n - 1)\mathrm{ROH}$$

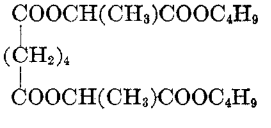
Thus in the esterification of adipic acid with butyl lactate, for instance, the alcoholic hydroxyl groups that react with the acid may be furnished by butanol, butyl lactate, butyl lactyllactate, or some higher polylactic ester. The situation is further complicated by the fact that dicarboxylic acids may form unsymmetrical esters with any two of the alcoholic compounds present.

Fractional distillation of the mixture of esters formed from adipic acid and butyl lactate resulted in the isolation of the principal components as relatively pure compounds:



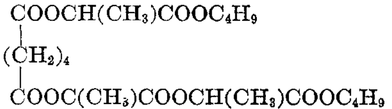
$$\begin{array}{l}\mathrm{COOC_4H_9}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{COOCH(CH_3)COOC_4H_9}\end{array}$$

Butyl (butyl lactate) adipate



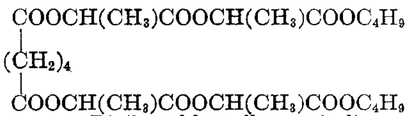
$$\begin{array}{l}\mathrm{COOCH(CH_3)COOC_4H_9}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{COOCH(CH_3)COOC_4H_9}\end{array}$$

Bis(butyl lactate) adipate



$$\begin{array}{l}\mathrm{COOCH(CH_3)COOC_4H_9}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{COOC(CH_3)COOCH(CH_3)COOC_4H_9}\end{array}$$

(Butyl lactate) (butyl lactyllactate) adipate



$$\begin{array}{l}\mathrm{COOCH(CH_3)COOCH(CH_3)COOC_4H_9}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{COOCH(CH_3)COOCH(CH_3)COOC_4H_9}\end{array}$$

Bis(butyl lactyllactate)adipate

These esters are shown in Table II with some properties of the crude mixtures of esters. The symmetrical esters, bis(butyl lactate) and bis(butyl lactyllactate) adipate were also prepared in pure form by use of adipyl chloride. The properties shown for these in Table II were determined on these pure samples (*5*). The unsymmetrical esters were isolated from the mixtures of esters obtained by use of adipic acid and hence were somewhat less pure.

Figure 1 is a Cox chart in which the boiling points $[1/(t + 273)]$ are plotted versus the pressure (log P), t being in ° C. and P in mm. This figure was a most useful guide in the distillation of the mixtures of esters obtained in the various experiments.

Study of Esterification Reaction. A brief study was made of the effect of several variables on the amount and kind of products formed in the acid-catalyzed esterification of butyl lactate with adipic acid. In these experiments the reactants were refluxed in a still having a 24-inch column packed with glass helices and having a water trap above the packing. Heating was begun at atmospheric pressure, steady reflux was maintained, water was removed as formed (butanol formed in the reaction served as an azeotropic agent to remove the water), and the reaction temperature was kept at or below 150° C. by suitably reducing the pressure from time to time as the reaction progressed. When reaction appeared complete, the catalyst was neutralized (preferably with a slight excess of powdered anhydrous sodium acetate), and butyl alcohol, lactate, lactyllactate, and adipate were removed successively by distillation at reduced pressure through a $1^1/_2 \times 24$ inch Vigreux column. The residue, after washing with dilute alkali and water, drying, and filtering, was suitable for use as a plasticizer.

The composition of the residue was estimated by distilling all or an aliquot portion in a high vacuum alembic still (*4*) and analyzing the fractions by boiling point and refractive index. Table III summarizes the results obtained in some selected typical experiments.

Experiments 1 and 2 (Table III) show that increasing the amount of catalyst markedly reduces the time required for reaction. The use of an equivalent amount of toluenesulfonic acid instead of sulfuric acid in several runs, including Expt. 10, made little difference in reaction time or color and composition of the product.

Comparison of the results of Expt. 2 with 3 or 8 with 9 shows that by increasing the proportion of butyl lactate in the reaction mixture above the theoretical amount, relatively more of the products boiling below bis(butyl lactate) adipate and less of the higher boiling products are produced.

The production of butyl adipate in the reaction mixture was undesirable because its high volatility necessitated its removal from the product before the latter could be used as a plasticizer. On the assumption that the composition of the reaction mixture approached a point of dynamic equilibrium, it was expected that addition of butyl adipate to the reaction mixture would reduce or prevent the formation of this compound during the reaction.

In Expts. 4 to 7, an increasing proportion of butyl adipate was

TABLE II. PROPERTIES OF ESTERS FORMED FROM ALKYL LACTATES AND DIBASIC ACIDS

Compound	Boiling Points, ° C.			n_D^{20}	d_4^{20}	Mol. Refraction		Sapon. Equiv.		Viscosity, Cp.	
	0.04 mm.	0.4 mm.	4.0 mm.			Calcd.	Found	Calcd.	Found	20° C.	40° C.
Butyl lactyllactate	51	80	117	1.4328	1.0631	53.21	53.34	...	...	16.20	6.69
Butyl adipate	77	109	147	1.4353	0.9615	70.16	70.17	...	...	....	...
Butyl (butyl lactate) adipate	110	145	188	1.4396	1.0175	85.67	85.50	110.1	108.3	15.55	7.80
(Butyl lactate)$_2$ adipate	141	177	220	1.4432	1.0543	101.18	101.24	100.6	99.7	41.37	16.56
(Butyl lactate) (butyl lactyllactate) adipate	166	202	246	1.4464	1.0922	116.68	115.96	94.9	94.2	177.1	46.68
(Butyl lactyllactate)$_2$ adipate	191	227	272	1.4470	1.1026	132.19	132.42	91.1	91.9	283.5	67.88
Crude butyl lactate adipate[a]	...	...	...	1.4418	1.0458	101.18	101.77	100.6	104.7	31.74	14.09
Capryl (capryl lactate) adipate	145	184	230	1.4432	0.9515	122.61	123.37	147.5	152.7	21.70	10.20
(Capryl lactate)$_2$ adipate	175	211	254	1.4446	0.9929	138.12	137.83	128.7	125.6	82.4	23.55
Crude capryl lactate adipate[b]	...	...	...	1.4438	0.9655	138.12	141.58	128.7	134.2	....	...
(2-Ethylhexyl lactate)$_2$ adipate	179	216	254	1.4494	0.9997	138.12	138.17	128.7	128.4	68.0	25.6
Crude 2-ethylhexyl lactate adipate	...	...	...	1.4485	0.9980	138.12	....	128.7	135.2	....	...
Capryl (capryl lactate) sebacate	170	207	252	1.4464	0.9442	141.09	140.95	166.3	163.3	45.6	19.50
(Capryl lactate)$_2$ sebacate	192	232	280	1.4475	0.9740	156.59	156.74	142.2	141.1	90.9	35.4
Crude capryl lactate sebacate[c]	...	...	...	1.4470	0.9440	156.59	160.99	142.2	152.4	66.6	26.5
Butyl (butyl lactate) maleate	90	125	169	1.4470	1.0524	75.97	76.30	100.1	99.8	22.66	9.65
(Butyl lactate)$_2$ maleate	123	158	201	1.4488	1.0852	91.48	92.01	93.1	93.8	74.3	19.36
Crude butyl lactate maleate[d]	...	...	...	1.4469	1.0727	91.47	92.74	93.1	95.5	....	...
Butyl (butyl lactate) phthalate	124	163	211	1.4863	1.0842	91.30	92.84	116.8	115.2	83.1	27.61
(Butyl lactate)$_2$ phthalate	155	191	237	1.4820	1.1094	106.81	108.56	105.6	105.6	283	69.0
Crude butyl lactate phthalate[e]	...	...	...	1.4852	1.093	106.81	110.80	105.6	109.2	....	...

Reaction product was topped to:
[a] 110° C. (vapor temp.) at 0.1 mm. (butyl adipate–free), washed, dried, and filtered.
[b] 100° C. (vapor temp.) at 0.2 mm. (capryl lactyllactate–free), washed, dried, and filtered.
[c] 175° C. (pot temp.) at 0.07 mm. (capryl lactyllactate–free), washed, dried, and filtered.
[d] 100° C. (pot temp.) at 1 mm., washed, dried, and filtered.
[e] 150° C. (pot temp.) at 0.3 mm., washed, dried, and filtered.

put into the reaction and, as expected, the amount formed decreased until, in Expt. 7, less butyl adipate was recovered in the product than had been put into the reaction mixture. It is evident, then, that butyl adipate can be recycled in the process so that none remains to be disposed of as a by-product. The same applies to any butyl lactate or lactyllactate recovered from the product.

In all experiments, small amounts of butyl lactyllactate adipates were recovered, and a distillation residue was obtained which probably consisted of higher polylactic esters. Because these polymeric esters were relatively less efficient as plasticizers than the monomeric lactic esters, their production in the esterification reaction was undesirable, and ways to prevent their formation were sought. In comparing Expt. 3 with 1 and 2, it was noted that increasing the proportion of butyl lactate used decreased the amount of high boiling polylactic esters and distillation residue, but only at the price of greatly increasing the amount of lactate and lactyllactate recovered. The unsymmetrical ester, butyl (butyl lactate) adipate, is a highly efficient plasticizer and is sufficiently high boiling for most applications, particularly when used in admixture with the higher boiling lactate adipates. Formation of this ester is favored and at the same time formation of polylactic esters is repressed by addition of butanol to the reaction mixture, as shown by the results of Expts. 8 and 9.

Since lactic acid is a commercially available raw material, it appeared desirable to combine the two esterifications, (*a*) lactic acid to butyl lactate and (*b*) butyl lactate to butyl lactate adipate, into a single step. This was done in Expt. 11, and it appeared that substantially the same result was obtained as when butyl lactate was first prepared separately.

According to a recent appraisal (*3*), the methanol vapor process (*2*) of purifying lactic acid is probably the most economical way to make high grade lactic acid. Hence, methyl lactate, an intermediate in this process, appeared to be potentially cheaper than lactic acid or butyl lactate. Expt. 12 was run to determine the feasibility of combining the two steps, (*a*) conversion of methyl lactate to butyl lactate and (*b*) esterification of butyl lactate with adipic acid, into a single step. Methanol was distilled from the reaction mixture as it was formed, after which water was removed as usual. The product was not significantly different from that prepared from butyl lactate or lactic acid.

Although it seemed evident that the general conclusions derived from the experiments in which adipic acid and butyl lactate were used would be valid for the use of other dicarboxylic acids and other alkyl lactates, a few experiments were run to verify this expectation. 2-Ethylhexyl lactate was esterified with adipic acid, capryl lactate was esterified with adipic and sebacic acids, and butyl lactate was esterified with maleic and phthalic anhydrides. In addition, an experiment analogous to 12, Table III, was run in which sebacic acid was reacted with ethyl lactate and capryl alcohol. No significant difference was noted in the reactivity of the various acids and anhydrides, but it was apparent that capryl alcohol and capryl lactate were less reactive in reactions involving the alcohol radical than the butyl compounds. The esters produced in these experiments are included in Table II.

The color of the reaction products depended to a great extent

TABLE III. ESTERIFICATION OF BUTYL LACTATE WITH ADIPIC ACID

Expt. No.	Reactants, Moles: Bu. Lactate	Adipic Acid	Bu. adipate	Bu. alc.	Catalysts, Grams H_2SO_4	Reaction Time, Hours	Products, Moles/Mole of Adipic Acid Used: Bu. lactate	Bu. lactyllactate	Bu. adipate[a]	Bu. (Bu. lactate) adipate	Bis(Bu. lactate) adipate	(Bu. lactate) (Bu. lactyllactate) adipate	Bis(Bu. lactyllactate) adipate	Total plasticizer[b], moles
1	2	1	0	0	0.2	12	0.19	0.10	0.23	0.22	0.21	0.14	0.07	0.64
2	2	1	0	0	1.0	5	0.17	0.10	0.23	0.28	0.27	0.07	0.04	0.66
3	4	1	0	0	1.0	2	1.45	0.52	0.33	0.43	0.22	0.06	0.01	0.72
4	8	4	1	0	4.0	1.5	0.20	0.08	0.29	0.34	0.20	0.18	0.04	0.76
5	6	3	1	0	3.0	6	0.11	0.05	0.05	0.43	0.28	0.13	0.04	0.88
6	4	2	1	0	2.0	4	0.16	0.07	0.07	0.38	0.27	0.11	0.04	0.80
7	2	1	1	0	1.0	4	0.17	0.08	−0.30	0.64	0.23	0.20	0.05	1.12
8	8	4	3	4	4.0	3	0.63	0.30	0.20	0.51	0.15	0.03	0.01	0.70
9	10	4	3	4	4.0	3	0.93	0.25	0.38	0.51	0.14	0.03	0.00	0.68
10	10	4	2	0	38[c]	4	0.28	0.16	0.02	0.50	0.31	0.12	0.05	0.98
11	8 (Lactic acid)	4	2	10	4.0	4	0.28	0.08	0.21	0.42	0.19	0.09	0.03	0.73
12	8 (Me. lactate)	4	2	10	4.0	6	0.17	0.07	0.08	0.49	0.26	0.11	0.01	0.87

[a] Net amount in excess of that put in.
[b] Total number of moles of ester distilled above butyl adipate.
[c] Toluenesulfonic acid.

TABLE IV. PROPERTIES OF PLASTICIZED POLYVINYL CHLORIDE–ACETATE[a]

Plasticizer	Tensile Strength, Lb./Sq. Inch	Ultimate Elongation, %	Modulus, (100% Elong.) Lb./Sq. Inch	Brittle Point, ° C.
2-Ethylhexyl phthalate (control)	3070	290	1500	−32
Butyl adipate	>2200	>390	700	−68
Butyl (bu. lactate) adipate	2620	320	920	−45
(Butyl lactate)$_2$ adipate	3060	330	1170	−30
(Butyl lactate) (butyl lactyllactate) adipate	3600	320	1565	−17
(Butyl lactyllactate)$_2$ adipate	3580	270	1910	−13
Mixed adipate esters, distilled[b]	3110	330	1120	−28
Mixed adipate esters, undistilled[c]	3145	315	1030	−35
Capryl adipate	2600	270	1140	−66
Capryl (capryl lactate) adipate	3110	270	1210	−44
(Capryl lactate)$_2$ adipate	3070	360	1270	−40
(Capryl lactate)$_2$ adipate, crude[d]	3350	250	1460	−36
(2-Ethylhexyl lactate)$_2$ adipate	3020	260	1255	−44
(2-Ethylhexyl lactate) adipate, crude[d]	2970	360	1530	−26
Capryl sebacate	2650	240	1190	−62
Capryl (capryl lactate) sebacate	2830	340	1400	−49
(Capryl lactate)$_2$ sebacate	2920	350	1230	−38
(Capryl lactate)$_2$ sebacate, crude[e]	2920	340	1460	−43
Butyl (butyl lactate) maleate	>3040	>380	1230	−35
(Butyl lactate)$_2$ maleate	>3240	>330	1670	−19
(Butyl lactate)$_2$ maleate, crude[f]	3620	350	1650	−17
Butyl phthalate	2670	340	980	−30
Butyl (butyl lactate) phthalate	3440	350	1580	−10
(Butyl lactate)$_2$ phthalate	3580	310	1800	1

[a] A 95:5 copolymer of vinyl chloride and vinyl acetate containing 35% plasticizer.

[b] All distillable material boiling above butyl adipate.

[c] Crude butyl lactate adipate topped to 110° C. (vapor temp.) at 0.1 mm. pressure (butyl adipate–free), washed, dried, and filtered.

Crude esters topped to:

[d] 100° C. (vapor) at 0.22 mm., washed, dried, and filtered.

[e] 175° C. (pot) at 0.07 mm., washed, dried, and filtered.

[f] 100° C. (pot) at 0.1 mm., washed, dried, and filtered.

on the purity of the materials used. When C.P. grade reagents were used, the sebacates were faintly yellow; the adipates were pale yellow to light brown; the maleates were a clear, medium brown; and the phthalates were a darker, reddish brown.

Decolorizing carbon was useful in removing some of the color but was found to be much more effective if added to the reaction mixture at the beginning of the esterification and filtered out after all processing had been completed. The use of 1% carbon by weight thus yielded clear, almost colorless products. Several brands of activated carbon were used, but no great differences in effectiveness were noted.

Free acidity in the reaction mixtures was followed by withdrawal and titration of samples. It could be reduced to around 1% (as acetic acid) by continuation of the esterification reaction until this value was reached. Further reduction was so slow as to be impractical. Neutralization of the catalyst with sodium acetate produced acetic acid. This was removed in stripping volatile materials from the product, thus further reducing free acidity.

A single wash with 1% sodium carbonate solution was sufficient to reduce the free acidity to around 0.02%, a value acceptable for most purposes. It was easy to wash the crude esters with the alkali if the initial acidity was not above 1 to 2%. However, if the acidity was as high as 3%, the wash was made tedious by the formation of emulsions.

Evaluation of Esters Obtained by Direct Esterification. Each of the esters isolated from the crude reaction products as well as the undistilled mixtures of esters was evaluated as a plasticizer for a commercial copolymer of 95% vinyl chloride and 5% vinyl acetate, as previously described (*7*). In each series of esters (Table IV) each additional lactic acid group introduced into the ester increased the tensile strength, modulus, and brittle point of the resin plasticized with it. Of course, the boiling points were increased at the same time, and this is of especial importance in the adipates and maleates.

In the butyl lactate adipate series of esters, it is apparent that dibutyl adipate is much too volatile, although extremely efficient as a plasticizer. Inclusion of one lactate group greatly reduces the volatility (boiling point about equal to that of hexyl phthalate) while retaining exceptional efficiency. The two lactate groups in bis(butyl lactate) adipate raise the boiling point further and produce a plasticizer equivalent to 2-ethylhexyl phthalate in volatility and low temperature performance and somewhat superior in producing compositions of low modulus. The esters of lactyllactic acid have extremely low volatility but are less efficient than those of monomeric lactic acid.

The same general trends are apparent in the other series of esters, the principal exception being that, with the exception of the maleates, the simple esters containing no lactic acid are sufficiently high boiling to permit them to be left in the undistilled plasticizer mixtures.

In the sebacate series, capryl sebacate is a highly efficient plasticizer but is of borderline compatibility. This defect is reduced or eliminated by the inclusion of lactate groups in the molecule, though at the expense of some loss in efficiency and low temperature flexibility.

Any commercial utilization of these products would probably be based on the use of the undistilled mixture of esters produced in the esterification reaction, after removal of the more volatile components. Hence, it was gratifying to find that these undistilled mixtures were as efficient as the distilled products and that the adipate and sebacate mixtures were equal or superior to 2-ethylhexyl phthalate in efficiency and permanence.

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