marked, as is adequately demonstrated by the data of Tables I and II. It must be concluded that tall oil esters have no place in the formulation of soluble-matrix paints, even at the lowest ester concentration (16%). Antifouling effectiveness is reduced somewhat below the standard with no compensating increase in the physical stability of the film. Formulations containing equal parts of rosin and tall oil ester result in films that possess an effective life of only 1 month and fail completely after 3 to 4 months. This failure is demonstrated further by the curves of Figures 1 and 2. On the theory of Ketchum and co-workers (*4*) that matrix solubility accounts for the functioning of this type formulation, an explanation of the data would lie in the fact that the solubility of the matrix is gradually reduced through the addition of insoluble ester to a point where sufficient amounts of copper to prevent fouling are no longer available at the paint-water interface. Aside from film solubility characteristics, a second factor probably contributes to the observed phenomena: Solutions of rosin produce grinding and wetting media which are relatively poor when compared with more highly regarded vehicles. Good pigment dispersion in rosin alone is difficult, and in such a medium the pigment particles may be conceived as being held in place in somewhat the same manner as bricks are held together with mortar. Thus, there are available comparatively large areas of pigment that may be exposed to the solvent action of sea water. On the other hand, an esterified rosin, or in this case, esterified tall oil assumes the characteristics of a fairly good grinding medium in which the pigment particles are well covered by envelopes of the matrix. Thus, the matrix must be penetrated or dissolved by the sea water before any copper from the enclosed particles may pass into solution. This concept appears to be justified by the facts as demonstrated by poor performance of the films containing large amounts of ester. Although rosin and presumably tall oil to a similar degree are soluble in sea water, they are fairly stable against rapid deterioration in contact with sea water. Poor physical stability of films high in ester indicates that in the higher concentrations the esters are subject to deterioration, manifested by a rapid physical breakdown which is obvious immediately in the degradation of the film. This is more pronounced in the case of the pentaerythritol ester than for glycerol.

In the formulations in which rosin was diluted with abietic acid and hydrogenated methyl abietate and even with an unesterified tall oil, performances approximately equal to rosin were obtained. This perhaps was not unexpected in view of structural similarities in each ingredient. The data on both physical properties and antifouling efficiency are somewhat more consistent with abietic acid and hydrogenated methyl abietate than for the tall oil blends which may be the result of their higher degree of purification and increased uniformity from batch to batch. Tall oil is somewhat less pure and uniform than rosin although its solubility and wetting properties are quite similar. For an exposure period of 10 months it is obvious that hydrogenated methyl abietate and abietic acid do not alter appreciably the performance of a rosin matrix regardless of the ratio of rosin to diluent. With tall oil alone, inferior performance is indicated when its percentage exceeds 70%. Below this figure paint prepared from tall oil rosin mixtures performed as efficiently as those containing normal amounts of rosin.

CONCLUSIONS

The data indicate that tall oil may replace up to 50% of the rosin normally present in a soluble-matrix type antifouling paint without affecting seriously the antifouling efficiency or physical stability of the film. Similarly, hydrogenated methyl abietate and abietic acid may be substituted for rosin up to 100% with a perceptible improvement in physical properties and equivalent performance as a fouling deterrent. Esters of tall oil, as illustrated by the glycerol and pentaerythritol derivatives, produce a marked adverse effect on soluble-matrix paints in direct proportion to the extent to which they are substituted. A copper pigment containing essentially 85% copper and 15% cuprous oxide does not quite equal cuprous oxide as an antifouling pigment in the matrices studied.

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N-Hydroxyalkyl Amides of Lactic Acid

PREPARATION AND PROPERTIES

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Seven *N*-hydroxyalkyl lactamides were readily prepared in high yield by aminolysis of methyl lactate with amino alcohols. These lactamides are water-soluble compounds of low volatility; six liquid lactamides had viscosities ranging from 4000 to 26,000 centipoises at 20° C. They varied widely in hygroscopicity; one, *N*,*N*-bis(2-hydroxyethyl)lactamide was more hygroscopic than glycerol. Because they can be considered as polyhydric alcohols, they may be useful chemical intermediates, as well as hygroscopic agents.

ALTHOUGH it has been reported that *N*-hydroxyalkyl amides of aliphatic (*9, 15, 17*), glycolic (*13*), and hydroxystearic acids (*10, 23*) are of industrial interest as waxes (*9, 10, 23*), plasticizers (*13, 18*), emulsifiers (*10, 15, 23*), and as humectants and thickening agents (*13*), apparently little attention has been directed to the *N*-hydroxyalkyl lactamides (*21, 25*).

In general, these lactamides can be prepared easily in high yield by the aminolysis of methyl lactate with amino alcohols; in the work reported here seven lactamides were prepared in this way (Table I). The starting materials are commercially avail-

Table I. Preparation and Properties of *N*-Hydroxyalkyl Lactamides

Lactamide	Yield, %	Viscosity at 20° C., Cp.	Distilling Temp., ° C. (Mm.)	Refractive Index, n_D^{20}	Density, d_4^{20}	Molecular Refraction Calcd.[a]	Molecular Refraction Obsvd.	Analyses C Calcd.	Analyses C Found	Analyses H_2 Calcd.	Analyses H_2 Found	Analyses N_2 Calcd.	Analyses N_2 Found
N-2-hydroxyethyl-	97	3,960	116-124(0.014-0.017)	1.4862	1.1860	32.21	32.24	45.1	45.0	8.3	8.4	10.5	10.7
N-3-hydroxybutyl-	97	10,000	130-139(0.005)	1.4777	1.1048	41.44	41.28	52.2	52.2	9.4	9.7	8.7	8.6
N-2-methyl-2-hydroxypropyl-[b]	99	...	102-111(0.005)	1.4737[c]	1.0984[c]	41.44	41.22	52.2	51.9	9.4	9.6	8.7	8.7
N-2-hydroxypropyl-	95	11,300	109-116(0.001-0.002)	1.4780	1.1339	36.82	36.75	49.0	48.2	8.9	9.0	9.5	9.4
N-ethyl-*N*-2-hydroxyethyl-	64[d]	1,260	105-114(0.003-0.007)	1.4800	1.1192	41.18	40.92	52.2	51.4	9.4	9.2	8.7	8.6
N,*N*-bis(2-hydroxyethyl)-	99[e]	25,900	...	1.5016	1.2282	42.70	42.54	47.4	47.9	8.5	8.5	7.9	7.7
N-(1,1-dimethyl-2-hydroxyethyl)-	86.5	25,600	101-107(0.008-0.030)	1.4728	1.0991	41.45	41.12	52.2	51.7	9.4	9.5	8.7	8.6

[a] The values 2.76 and 2.49 were used for the atomic refractions of nitrogen in the amides from primary and secondary amines, respectively (*3*, *22*); the usual values were used for the other atoms (*7*).
[b] Melting point, 70.5° to 71.5° C.
[c] For the undercooled liquid.
[d] Crude product. Analytical data and constants are given for one fraction.
[e] Residue.

able. The lactamides are water-soluble materials of low volatility and pronounced hygroscopicity; *N*,*N*-bis(2-hydroxyethyl)-lactamide is more hygroscopic than glycerol.

These properties suggest that the *N*-hydroxyalkyl lactamides may be useful as softening agents, humectants, and water-soluble plasticizers. Moreover, because these amides have two or more unsubstituted hydroxy groups, they can be considered polyhydric alcohols, and may be useful intermediates in making ester gum and alkyd resins, and various esters. Probable future reductions in the cost of lactic acid (*5*, *16*) may make them especially attractive for industrial use.

PREPARATION

Materials. The methyl lactate, obtained commercially, was redistilled in vacuum (Vigreux column). It was optically inactive.

The amines were obtained from commercial sources; most of them were stored over potassium hydroxide for a few days, then filtered and distilled in efficient columns. The properties of the amines are listed in Table II.

Table II. Physical Constants of Hydroxy Amines

Amine	Boiling Point, ° C. (Mm.)	Refractive Index, n_D^{20} Obsvd.	Refractive Index, n_D^{20} Lit.	Neutral Equivalent Obsvd.	Neutral Equivalent Calcd.
3-Hydroxybutyl-	122.5-123 (101)	1.4530	1.453[a]	...	...
2-Hydroxypropyl-	86 (37)	1.4478	1.4478[a]	75.3	75.1
2-Hydroxyethyl-	166 (760)	1.4538	1.4539[b]	61.6	61.1
Diethanol-	139.5-140 (5)	1.4972	1.4776[b]	105.7	105.1
2-Amino-2-methyl-1-propanol-	99.5-100 (58)	1.4487	...	90.1	89.1
Ethylethanol-	162.5 (752)	1.4408	1.4407[a]	90.0	89.0
2-Methyl-2-hydroxypropyl-	......	1.4465	1.446[a]	...	...

[a] Information supplied by the manufacturer.
[b] See reference (*11*).

Aminolysis. The reaction is illustrated by the formation of *N*-2-hydroxyethyl lactamide:

$$CH_3CHOHCOOCH_3 + CH_2OHCH_2NH_2 = CH_3CHOHCONHCH_2CH_2OH + CH_3OH$$

The experimental technique was similar to that previously described (*19*); the amine was mixed with a 10% excess of ester and the reaction followed by periodic titration. Methanol was distilled away and then the lactamides were distilled in high vacuum, because the amides appeared to be somewhat sensitive to heat. The yields in Table I refer to the distilled product, except as noted. Of seven lactamides prepared, six were viscous liquids; the seventh was solid at room temperature but distilled satisfactorily and remained an undercooled liquid long enough to permit density and refractive index measurements (Table I). *N*,*N*-bis-(2-hydroxyethyl)lactamide was not successfully distilled, even in a centrifugal molecular still (*1*). When care was taken to keep the temperature below 60° C. during removal of methanol and excess ester, it was obtained as a pale yellow residue.

Glycolamides. *N*-2-hydroxyethylglycolamide was obtained as a dark colored crystalline residue by aminolysis of methylglycolate. A portion was recrystallized several times from acetone prior to analysis. *N*,*N*-bis(2-hydroxyethyl)glycolamide was obtained as a crude dark nondistillable residue.

HYGROSCOPICITY

The data on the equilibrium compositions of the lactamide samples at various relative humidities were determined in a constant temperature room at 25° C. in apparatus of the type described by Wink (*26*) and also according to the method of McKee and Shotwell (*12*).

To check the accuracy of the determinations, the hygroscopicities of glycerol and sorbitol (Arlex) were determined concurrently and compared with the reported data (*8*); the agreement was excellent.

Saturated solutions of the following salts were used to provide constant humidity (*2*, *24*); the relative humidity at 25° C. is indicated in parentheses—potassium acetate (22.5%), magnesium chloride hexahydrate (32.5%), potassium nitrite (48%), sodium nitrite (64.5%), and sodium chloride (75.5%). Equilibrium compositions computed as weight per cent of amide were plotted against humidity, and a smooth curve was drawn through the points (Figure 1). Table III lists the observed equilibrium compositions.

In three series of experiments, 5-gram samples (weighed to the nearest 0.5 mg.) in beakers 50 mm. in diameter were stored in a

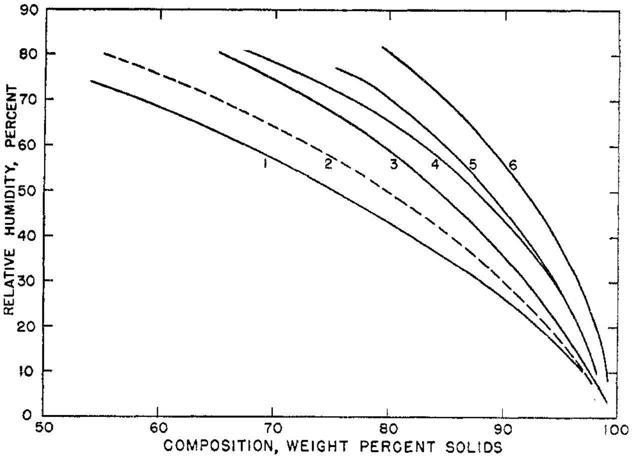

Figure 1. Equilibrium Hygroscopicity

1. ***N*,*N*-bis(2-hydroxyethyl)lactamide**
2. **Glycerol**
3. ***N*-2-hydroxyethyllactamide, sorbitol**
4. ***N*-2-hydroxypropyllactamide**
5. ***N*-3-hydroxybutyllactamide**
6. ***N*-(1,1-dimethyl-2-hydroxyethyl)lactamide**

large desiccator containing one of the saturated salt solutions. Each sample was weighed daily to the nearest 0.5 mg. until the composition changed less than 0.1% in 24 hours. This composition was taken as the equilibrium value, and the sample was then transferred to another desiccator; the successive humidities to which each sample was exposed were selected at random. *N*,*N*-bis(2-hydroxyethyl)lactamide displayed pronounced hysteresis. It was observed, however, that in each series the equilibrium compositions reached at humidities approached from below were in good agreement, and these values were used in constructing curve 1 of Figure 1.

TABLE III. EQUILIBRIUM COMPOSITIONS AT 25° C. OF HYDROXYALKYL LACTAMIDES

(Expressed as weight per cent of amide)

Curve No. (Figure 1)	Lactamide	Per Cent Amide at Relative Humidities of 22.5%	32.5%	48%	64.5%	75.5%
1	*N*,*N*-bis(2-hydroxyethyl)-[a]	91.8	86.8	78.2	62.8	54.0
3	*N*-2-hydroxyethyl-	94.7	91.5	86.0	77.0	67.1
4	*N*-2-hydroxypropyl-	95.7	93.5	88.7	81.0	72.4
5	*N*-3-hydroxybutyl-	96.1	94.2	89.5	82.5	75.5
6	*N*-(1,1-dimethyl-2-hydroxyethyl)-	97.3	95.5	92.4	87.3	81.4

[a] These data were observed for increasing humidities.

Reproducibility for *N*-ethyl-*N*-2-hydroxyethyllactamide and crude *N*,*N*-bis(2-hydroxyethyl)glycolamide was not good, and no data are reported for these compounds. The other compounds (Table III) attained the same composition whether the humidity was approached from above or below. *N*-2-hydroxyethylglycolamide reached a composition of 98% at 48% relative humidity, and 90% at 64.5%. It was not investigated further.

The relatively long times (3 to 6 weeks) required for reaching equilibrium by the method described here led to the use of 2-gram samples distributed on Pyrex glass No. 774 wool mats in the dishes of the Wink apparatus. Equilibrium was reached much more rapidly (1 to 2 weeks); the data for compounds run by both methods were in good agreement.

The optical activity of lactic acid derivatives has a pronounced effect on the hygroscopicity of these compounds. *d*-Lactamide (melting point 49° to 51° C.) is extremely hygroscopic (*6*), whereas *dl*-lactamide (melting point 76.4° C.) is stable (*14*). On the other hand, *dl*-*N*,*N*-dimethyllactamide acetate (melting point 34° to 35° C.) deliquesces in air (*20*), but *l*-*N*,*N*-dimethyllactamide acetate (melting point 60° to 61° C.) is stable (*20*). The amides of the present paper were optically inactive. The hygroscopicities of the corresponding amides made from *d*- or *l*-lactic acid (not commercially available) are not known.

DISCOLORATION OF *N*,*N*-BIS(2-HYDROXYETHYL)LACTAMIDE. The brown color developed during exposure of this compound to moist air in the hygroscopicity determinations was caused by oxygen.

An accelerated aging test at 80° to 90° C. was devised in which moist air was passed through samples containing 0.1 to 0.5% by weight of various possible inhibitors. Sodium bisulfite was the most effective one tried: no color developed in a sample containing 0.2% of this inhibitor for 3 days (the period of the test), but an untreated sample turned dark brown.

Less effective were sodium sulfite, sodium nitrite, and sodium hydrosulfite.

PHYSICAL PROPERTIES

The viscosity, refractive index, and density of each compound were determined by described methods (*4*). The high viscosities of *N*,*N*-bis(2-hydroxyethyl)lactamide and *N*-(1,1-dimethyl-2-hydroxyethyl)lactamide suggest that materials plasticized with those compounds would not become limp and soggy, even at high humidities.

The distilling temperatures in Table I, although not true boiling points, indicate that the lactamides are about as volatile as di-2-ethylhexyl phthalate, which has a vapor pressure of 0.005 mm. at 112° C. and 0.02 mm. at 130° C.

All the *N*-hydroxyalkyl lactamides are insoluble in ether and benzene.

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