Peaked Distribution Ethoxylates–Their Preparation, Characterization and Performance Evaluation[1]

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A peaked ethylene oxide distribution alcohol ethoxylate can be produced using new catalyst systems. The mechanism of ethoxylation is discussed. Such Novel™ ethoxylates are markedly different from a conventional ethoxylate in physical properties and performance characteristics. Performance and formulation studies show several advantages for the peaked distribution in typical household product formulations.

Conventional base catalyzed ethoxylates of primary alcohols are composed of a broad distribution of ethylene oxide (E.O.) adducts as shown in Figure 1. It has been recognized by the detergent industry that both processing and performance advantages could be gained by reducing the levels of the free alcohol, the low mole and the extra high mole E.O. adducts (1-3).

One way to produce such materials was to physically strip out the low mole E.O. adducts after ethoxylation (1). However, we have identified several difficulties with this approach. First, there were added energy and equipment costs due to the stripping. Then, recycling of free alcohol and low mole adducts gave rise to both color and odor problems in the final product. Finally, the stripped ethoxylate itself had a distribution skewed toward the higher E.O. adducts which, in some liquid applications, do not give optimum formulation and performance properties. These factors added up to a significant cost penalty for the stripped ethoxylates. Due to poor cost/performance, the stripping out of the volatile low mole E.O. adducts, as a means for achieving a more peaked distribution, was not considered very promising.

In 1978, Conoco began working on peaked distribution ethoxylates. Instead of using the previously described engineering approach, we chose a chemical approach to solving the problem. This approach focused on developing improved catalyst systems for the ethoxylation reaction itself. In this way, the E.O. adduct distribution could be peaked to minimize the levels of both low mole and high mole E.O. adducts and to maximize the level of E.O. adducts in the desired range. Our intent was to make this product at little or no additional cost to the detergent manufacturer compared to conventional ethoxylates.

EXPERIMENTAL

Detergency tests in this study were run according to Vista CTS Lab Method No. 303-84, which is similar to ASTM Method No. D3050-75. The smoke point tests were run using a modification of AOCS Official Method Cc 9a-48.

All the nonionic samples tested were prepared from linear primary alcohols. The ethoxylates were generally a blend of C12 and C14 carbon chain length alcohols ethoxylated to the indicated weight percent E.O. level using various catalysts.

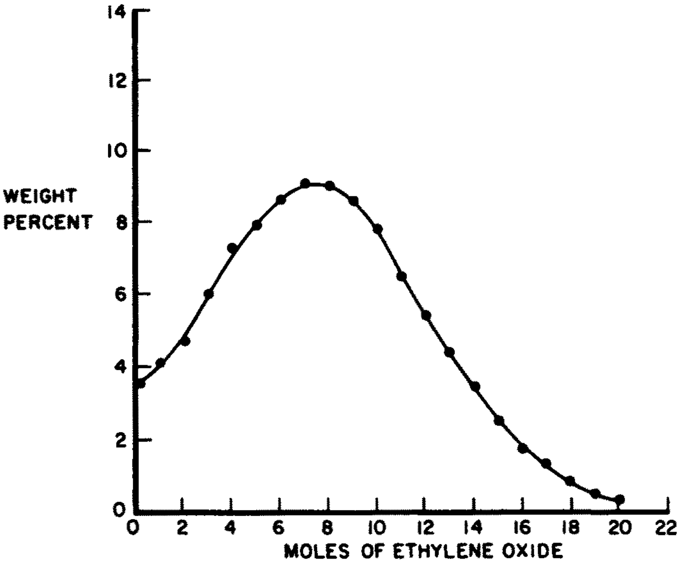

FIG. 1. Typical E.O. adduct distribution for a conventional base-catalyzed alcohol ethoxylate averaging about 7 moles E.O.

The E.O. adduct distributions were determined using the HPLC method developed by Linder and Allen (4). The free unethoxylated alcohol was determined by GC. We believe the HPLC method gives the most realistic E.O. distributions because it is sensitive enough to detect the individual E.O. adducts from one mole up to above 20 moles. We found the GC approach for determining E.O. distribution to be unacceptable because of gradually declining sensitivity to ethoximers as the E.O. adduct level increased (M. A. Allen, private communication).

ETHOXYLATION MECHANISMS

It has been suggested that the broad distribution of E.O. adducts obtained with alkali metal base catalyzed ethoxylation resulted from the small difference in the acidity of alcohol and ethoxylated alcohol (5,6):

$$RO^- + ROCH_2CH_2OH \rightleftharpoons ROH + ROCH_2CH_2O^- \quad [1]$$

The equilibrium for this reaction is shifted to the right, indicating the presence of more ethoxylated alkoxide anions than unethoxylated ones. Ethoxylated alcohols thus react faster with ethylene oxide than the starting alcohol, and an appreciable amount of higher mole E.O. adducts is produced even when a considerable amount of unreacted alcohol still remains. Presumably this is the reason why in some conventional ethoxylates there is more free alcohol than the one mole E.O. adduct.

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[1] Presented at the AOCS meeting in Dallas, May 1984.

[2] Deceased.

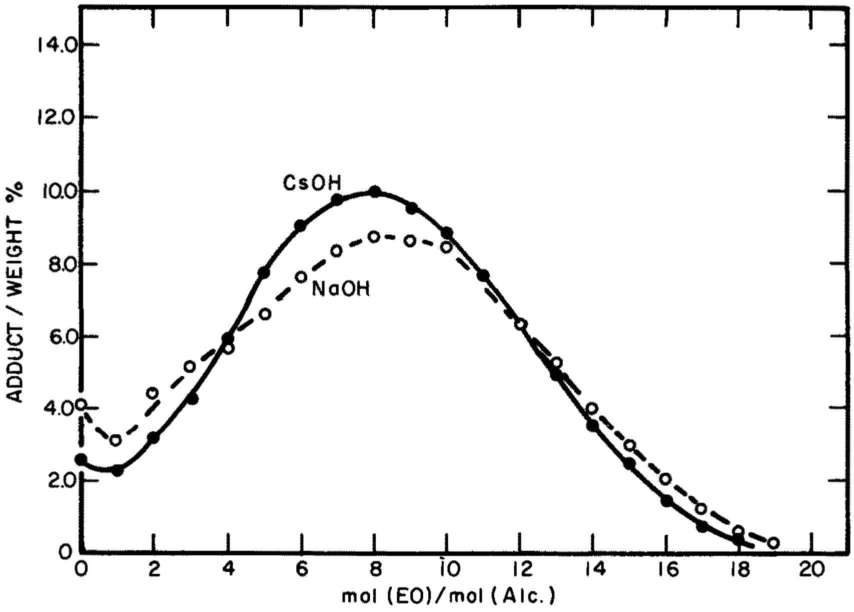
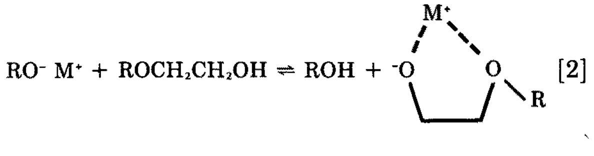


FIG. 2. E.O. distribution of Alfonic® 1214-60.

This acidity mechanism is consistent with the experimental observation that the distribution tends to sharpen as the base strength of the catalyst increases from NaOH to CsOH, as shown in Figure 2. With a stronger base, the acidity difference between alcohol and ethoxylated alcohol becomes less significant.

During the course of this catalyst research, it was discovered that ethoxylation with weaker bases such as alkaline earth hydroxides can produce a distribution even sharper than that obtained with a strong base such as KOH. An example is shown in Figure 3. This result was completely unexpected and prompted some rethinking of the previously discussed mechanism, which was based on acidity differences. A new mechanism was proposed which modifies equation [1] by incorporating the metal cation-alkoxide anion interactions:



[2]

With alkali metal bases this mechanism would predict results similar to equation [1]. However, with divalent metal cations, there will be two bulky ethoxylated alkoxide anions surrounding the metal ion. This overcrowding should reduce the interaction between the cation and the ether oxygen. Then the equilibrium shift to the right is less significant and the resulting product is expected to have a more peaked E.O. adduct distribution.

The result is an ethoxylate with a nearly symmetrical peaked distribution containing more of the desired midrange E.O. adducts and less of the low mole and high mole E.O. adducts. Because this is an improvement in ethoxylation catalyst technology, peaked distribution ethoxylates of any E.O. level can be prepared. Examples of peaked distribution ethoxylates compared to corresponding conventional NaOH catalyzed ethoxylates of similar weight percent E.O. level are shown in Figures 3 to 5. Table 1 lists comparative analytical data for peaked and regular distribution Alfonic® 1214-58. Generally, little difference is observed except in the hydroxyl number and the free alcohol level.

This work has resulted in several patents and publications which discuss some of the details of preparation (7-13). More importantly, it has led to the development of peaked distribution nonionic which has been produced commercially for several years. We differentiate the peaked distribution nonionics from our conventional Alfonic® ethoxylate products by the designation of Novel™ ethoxylates.

PERFORMANCE AND PROCESSING ADVANTAGES

Novel™ ethoxylates, i.e., alcohol ethoxylates having a peaked distribution of ethylene oxide adducts, offer several advantages over conventional ethoxylates: (i) greater liquidity of the nonionic; (ii) improved processability of the nonionic in laundry products; (iii) improved formulatability in liquid detergent products, and (iv) improved detergency performance in laundry products (12,13).

Because of the peaked distribution, the Novel™ ethoxylates exhibit lower pour points than corresponding conventional ethoxylates, as shown in Table 2. This tendency toward greater liquidity indicates some possible energy cost savings for the Novel™ ethoxylates in industrial storage and handling.

A major processing advantage for Novel™ ethoxylates is in the spray drying manufacture of nonionic-based laundry powders (14). Such laundry products, when spray dried, have a tendency to form a smoky plume emanating upward from the spray tower and usually incurring the displeasure of local regulatory agencies. This pluming is caused by the volatilization of the lighter components in the ethoxylate (14). Because Novel™ ethoxylates contain less free alcohol and low mole E.O. adducts, they show a significantly reduced pluming tendency compared to regular ethoxylates.

The tendency for an ethoxylate to plume is approximated by the smoke point test (a modification of AOCS Official Method Cc 9a-48). Table 3 shows the comparison between smoke point values and free alcohol levels of Novel™ and regular ethoxylates. This reduced pluming tendency offers the advantage of increased production efficiency in a spray drying operation.

Novel™ ethoxylates show advantages over conventional ethoxylates in formulating heavy duty liquid detergent products. The peaked distribution contains less free alcohol and low mole E.O. adducts which are not very soluble in water. As a result, stable formulations can be

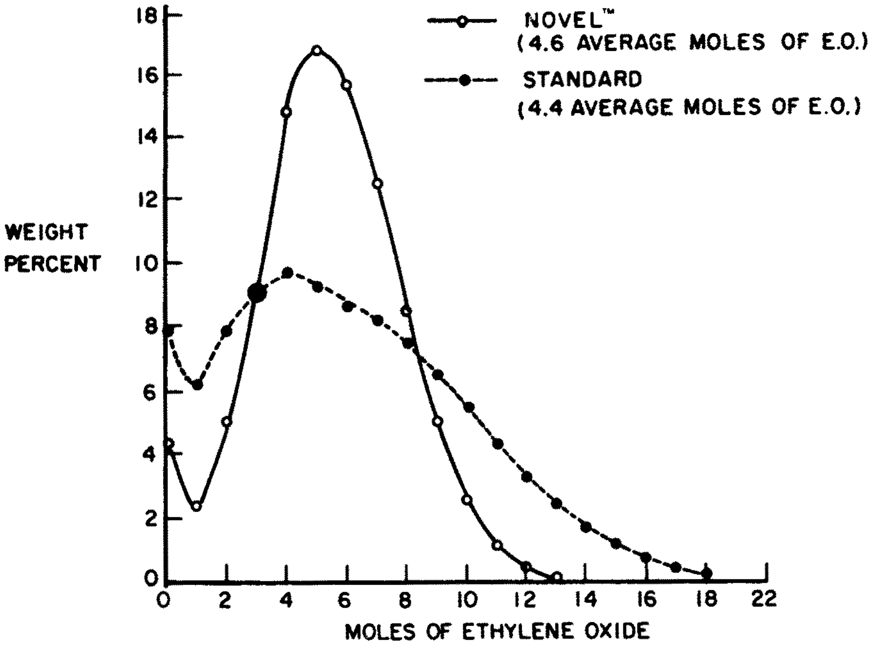


FIG. 3. E.O. distribution of Alfonic® 1214-50.

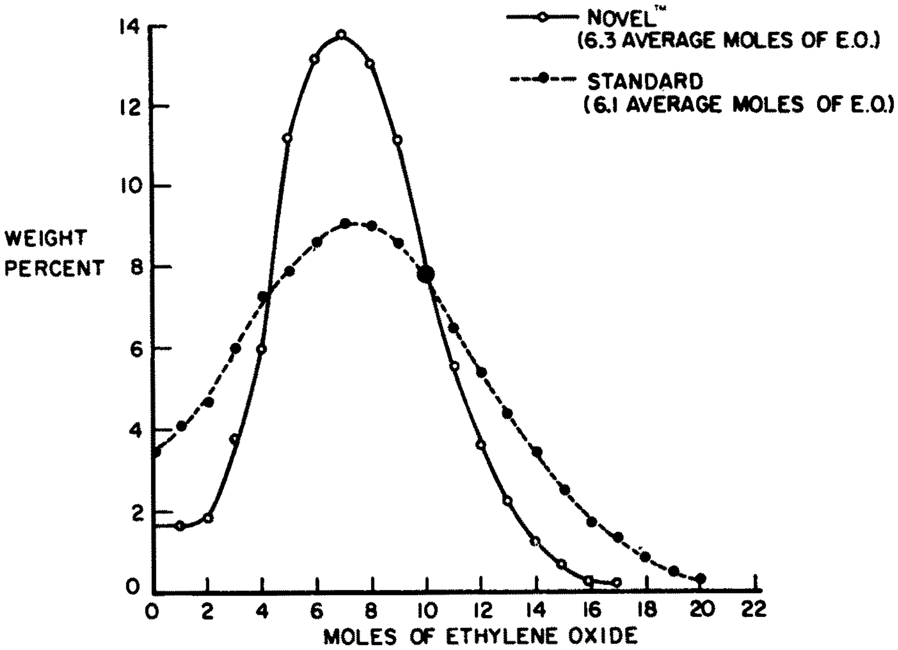


FIG. 4. E.O. distribution of Alfonic® 1214-58.

made from these ethoxylates over a broader range of percent E.O. levels than with regular ethoxylates, as indicated in Table 4. Also, the peaked distribution contains less of the high mole E.O. adducts which may not be readily soluble in nonaqueous solvents. Hence the Novel™ ethoxylates could exhibit formulation advantages over regular nonionics in solvent-based cleaners.

Another area of liquid detergent products where the Novel™ ethoxylates show formulation advantages is that of combination laundry liquids containing fabric softener and detergent. These products may contain high levels of nonionic and cationic surfactants and usually re-

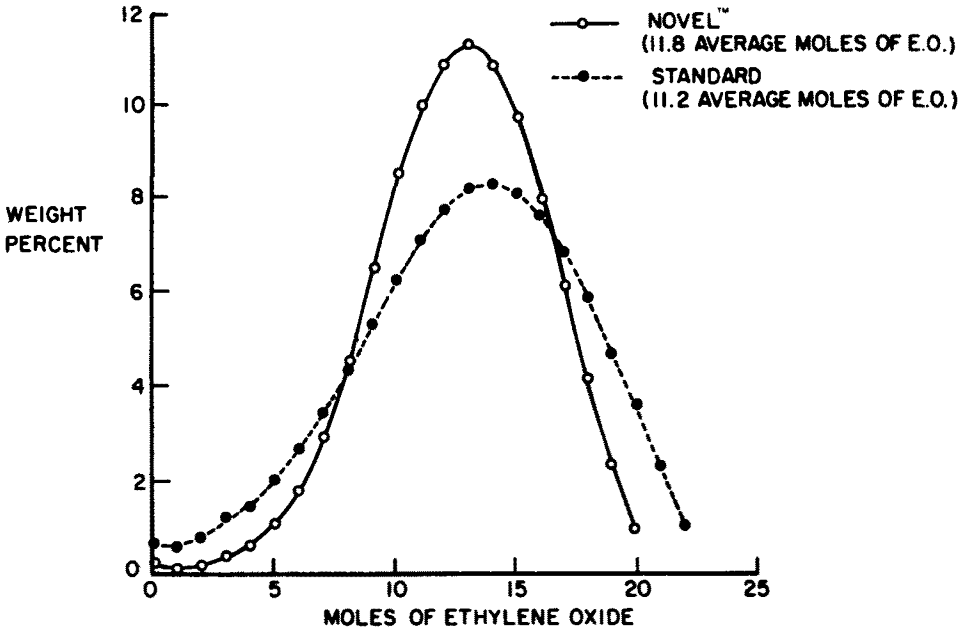


FIG. 5. E.O. distribution of Alfonic® 1214-70.

TABLE 1

Comparative Analysis of Peaked and Regular Distribution Alfonic® 1214-58

	Peaked	Regular
Hydroxyl number	114.3	122.8
Glycol, weight percent	.5	1.4
Ethylene oxide, weight percent	57.7	57.2
Average E.O. adduct, moles	6.3	6.1
Water, weight percent	0.06	0.09
APHA color	40	30
Free alcohol, weight percent	1.70	3.47

TABLE 2

Pour Point Values for Novel™ and Conventional Ethoxylates[a]

	Pour point
Novel™ 1214 GC-60 ethoxylate	60 F
Alfonic® 1214 GC-60 ethoxylate	70 F

[a]The ethoxylates tested were made from a 70/30 blend of C12/C14 linear primary alcohols ethoxylated to 60% by weight (approximately 6.5 mole average) of ethylene oxide.

TABLE 3

Ethoxylates[a] **for Spray Drying**

	Alfonic® 1418-		Novel™ 1418-	
	67	72	67	72
Hydroxyl number	79	66.9	80.4	62.0
Ethylene oxide, weight percent moles	67.1	72.3	66.7	71.9
Free alcohol, weight percent	0.94	0.35	0.35	0.14
Smoke point, °F	295	312	315	325

[a]Made from a blend of C14, C16 and C18 linear, primary alcohol ethoxylated to 67% and 72% by weight E.O., respectively.

TABLE 4

Viscosity and Cloud/Clear Data for a Typical Nonbuilt HDL Formulation (35% NI/10% LAS/5% EtOH/1% KCl)

Nonionic[a]	Viscosity (in cps at 77 F)	Cloud/ Clear (in °F)
Alfonic® 1214 HB-55	2 Phase	2 Phase
Novel™ 1214 HB-55	127	14/16
Alfonic® 1214 HB-60	201	30/36
Novel™ 1214 HB-60	181	35/37

[a] The nonionics are made from an 80/20 blend of C12/C14 linear primary alcohol and ethoxylated to levels of 55% and 60% E.O. by weight, respectively.

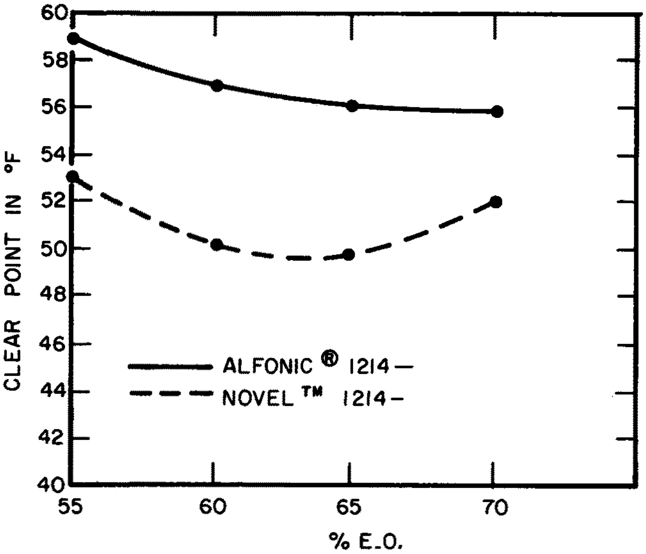


FIG. 6. Clear point temperatures for HDL formulation containing 25% nonionic/4% softener (dialkyl dimethylammonium chloride)/10% EtOH.

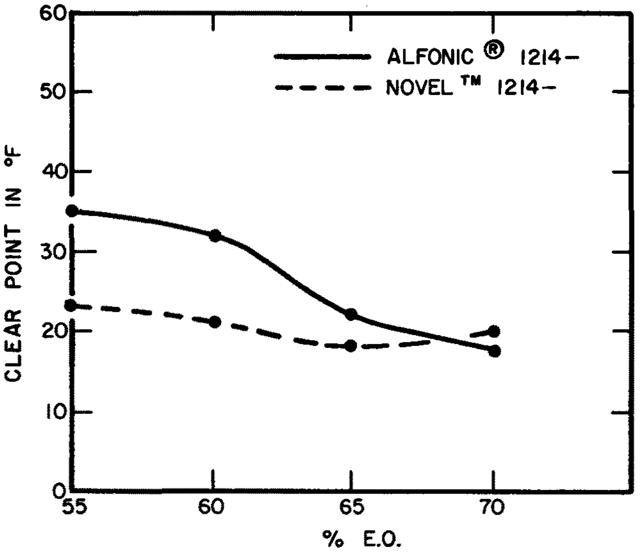


FIG. 7. Clear point temperatures for HDL formulation containing 25% nonionic/4% softener (oleyl immidazolinium methosulfate)/10% EtOH.

quire fairly high amounts of hydrotrope (ethanol or isopropanol in order to provide formulation stability). Figures 6 and 7 show that the Novel™ ethoxylates require less hydrotrope than regular ethoxylates (as measured by cloud/clear point temperature stability) in a typical combination detergent/fabric softener formulation, and consequently offer a hydrotrope cost savings advantage.

Although sebum/dust soiled cloth probably is the most widely used test soil, detergency performance tests show that oily soils are much more sensitive in their response to the level of E.O. on the nonionic. In particular, the 0, 1, 2 and 3 mole E.O. adducts give much poorer performance on oily soils than the 4 and higher mole E.O. adducts (15). For this reason, in typical nonionic-based laundry products, peaked distribution ethoxylates generally show better detergency than corresponding regular ethoxylates on oily soils, because they contain substantially less of the low mole E.O. adducts. Table 5 shows detergency data on mineral oil soil for a typical NI/LAS-based HDL containing both peaked and regular ethoxylates of both C12 and C14 linear primary alcohols. The level of ethoxylation ranges from 40 to 60%.

On sebum-soiled cotton and permanent press cloth, the detergency performance of the Novel™ and regular distribution ethoxylates is generally similar.

Another example of a formulation where these detergency advantages are particularly noticed is the combination detergent/fabric softener heavy-duty liquids containing nonionic and a quaternary ammonium salt. The detergency data (Table 6) show significant advantages for the peaked distribution ethoxylate, especially at the 55% E.O. level.

In summary, peaked distribution ethoxylates can be produced by improved ethoxylation catalyst technology. Such ethoxylates exhibit different physical properties and several improved performance characteristics compared to conventional nonionics. Our research on ethoxylation is continuing. Samples have been prepared with even more sharply peaked E.O. distributions (Fig. 8). These samples have a much narrower distribution of E.O. adducts and contain even lower levels of free alcohol than existing commercial peaked distribution ethoxylates.

TABLE 5

Detergency on Mineral Oil Soiled Perma Press Cloth[a]

	Y reflectance values	
Nonionic	Peaked	Regular
12-40	55.8	54.8
12-50	58.6	56.7
12-60	59.4	56.7
14-40	54.5	54.9
14-50	57.0	55.8
14-60	57.4	56.6
Least Significant Difference	.79	

[a] 100 F, .1% conc, 150 ppm hardness, 35% nonionic/10% LAS.

TABLE 6

Detergency on Mineral Oil Soiled Perma Press Cloth[a]

	Y reflectance values	
	50 ppm	150 ppm
Novel™ 1214 HB-55	62.4	64.4
Novel™ 1214 HB-60	63.8	65.3
Novel™ 1214 HB-65	62.4	63.5
Alfonic® 1214 HB-55	57.8	61.3
Alfonic® 1214 HB-60	61.7	64.3
Alfonic® 1214 HB-65	61.8	62.2
Least significant difference	1.3	1.0

[a] 100 F, .2% conc, 50 and 150 ppm hardness, 25% nonionic/4% dialkyl dimethyl ammonium chloride.

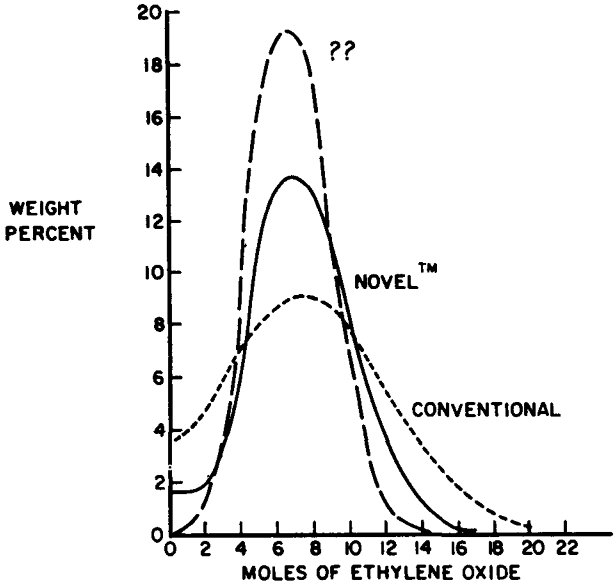


FIG. 8. E.O. distributions for conventional, Novel™, and future peaked distribution ethoxylate.

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