⁂Reduction in Pluming During the Spray Drying of a Nonionic-Based Heavy Duty Powder

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The plume observed during the spray drying of a nonionic-based heavy duty powder has been attributed to volatilization/recondensation of unethoxylated alcohols and other components in the alcohol ethoxylate. These "volatile components" comprise only 24–40% of the total spray tower emissions, but they are responsible for 85–95% of the observed opacity. Therefore, the relationship between observed opacity of the plume and particulate loading is not valid for the exhaust air from a spray tower producing nonionic-based powdered detergents. Alcohol ethoxylates are not decomposed to any measurable amount in a typical spray-dryer operation. The relative pluming tendency of alcohol ethoxylates depends exclusively on their relative vapor pressure. The vapor pressure of an alcohol ethoxylate is a function of the hydrophobe composition (starting alcohol) and the degree of ethoxylation which determines the level of unethoxylated alcohols. A new generation of alcohol ethoxylates with 60% less unethoxylated alcohol for a given ethoxylation level has been introduced recently. These Novel™ alcohol ethoxylates result in drastically improved pluming characteristics.

The spray drying of heavy duty detergents containing high levels of nonionic surfactants (alcohol ethoxylate) can result in excessive smoking or pluming in the exhaust air from the tower. The plume (smoke) is the noticeable reduction in light transmission caused by light scattering and absorption by particulates in the exit gas. (Particulate is defined as "materials which are solid or liquid phase in the spray tower exhaust prior to leaving the stack.") The particulate loading and plume opacity are two measures monitored by regulatory agencies concerned with air quality. The ease of visually monitoring the plume opacity has made it a critical environmental standard for spray towers.

However, the relationship between plume opacity and particulate loading is very complex. The presence of a high plume opacity does not necessarily mean excessive particulate loading. The converse of this is also true. The identification of the components in the exhaust air and their origin would help to better understand the reason for high plume opacity during the spray drying of nonionic-based powders.

The materials in the exhaust air of a spray tower may originate via three mechanisms, (i) particulate carryover; (ii) organic component (nonionic) degradation to volatile components which condense after exiting the stack, and (iii) volatilization of components present in the feedstocks. Particulate carryover is reduced via elaborate cyclones, scrubbers and other means to meet air quality standards. The degradation of nonionics has been the focus of most previous work on this problem (1,2). Elaborate lab tests have been designed to induce nonionic degradation and attribute pluming to this factor.

Identification of the components emitted from a spray tower and quantification of their relative contribution to pluming would yield the origin of the observed plume. Only one previous published report (3) has attempted to identify the components in the exit gas.

EXPERIMENTAL

Materials. The nonionic utilized during the stack sample collection was a linear alcohol ethoxylate containing dodecanol, tetradecanol, hexadecanol and octadecanol ethoxylated with an average of 9.5 mol of ethylene oxide/mol alcohol (Table 1). The peaked linear ethoxylate contained dodecanol and tetradecanol with an average of 11.2 mol ethylene oxide/mol alcohol (Table 2). The peaked ethylene oxide distribution was made via a proprietary catalyst system (4). The remainder of the powder formulation consisted mainly of sodium sulfate and sodium tripolyphosphate.

Stack gas sample collection. The stack gas samples were collected utilizing the apparatus described in EPA Method No. 5 (5) with two alterations. Methylene chloride was used as the solvent in the first two wet traps instead of water. This eventually resulted in plugging the second trap (~38 min into the test run) because of freezing of the water contained in exhaust gas as a result of methylene chloride evaporation. The methylene chloride was replaced with water, and the test continued. The second alteration was the use of glass beads in the third impinger, which normally is empty. The samples were separated into the probe wash (a); cyclone, filter holder, and filter

TABLE 1

Alcohol Ethoxylate Analysis

Test	Result
Alcohol distribution (100% ROH basis, wt%)	
Decanol	0.7
Dodecanol	25.2
Tetradecanol	22.1
Hexadecanol	32.3
Octadecanol	19.7
Average alcohol MW	222.8
Average moles of ethylene oxide per mole of alcohol	9.5
Free alcohol, wt%	
Decanol	0.04
Dodecanol	0.47
Tetradecanol	0.41
Hexadecanol	0.37
Octadecanol	0.25
Total	1.54

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TABLE 2

Peaked Distribution Alcohol Ethoxylates

Test	Result
Alcohol distribution (100% ROH basis, wt%)	
Decanol and lower	0.4
Dodecanol	30.0
Tetradecanol	68.7
Hexadecanol	0.9
Average alcohol MW	205.0
Moles of ethylene oxide per mole of alcohol	11.2
Free alcohol, wt%	
Decanol	—
Dodecanol	0.06
Tetradecanol	0.14
Total	0.20

TABLE 3

Composition of Materials in Exhaust Air from Spray Tower (mg/m^3)

Component	Probe (a)	Filter/ Cyclone (b)	Wet train (c)	TOTAL
Sodium sulfate	72.3	1.4	<2.2	75.9
Sodium tripolyphosphate	1.0	0.5	0.9	2.4
Alcohol ethoxylate	3.8	—	—	3.8
Volatile organic^a	—	—	58.2	

^{a}Volatility equal to or greater than *n*-hexadecanol.

TABLE 4

Composition of Organic Fraction

Componet	Amount (mg/m^3)	Relative percent
Decanol	2.5	4.3
Dodecanol	17.5	30.1
Tetradecanol	8.0	13.8
Hexadecanol	3.1	5.3
1-Ethoxy-dodecanol	5.5	9.4
Total alcohol derived	36.6	62.9
n-Paraffins	16.2	27.9
Unidentified	5.4	9.2
Total $\leqslant$*n*-hexadecanol	58.2	100

TABLE 5

Predicted Ratio of Alcohols (Raoult's Law)

Component	Relative percent in initial product	Plume relative percent (Raoult's Law)	Actual relative percent
Decanol	2.5	14.4	6.8
Dodecanol	29.4	54.7	47.9
Tetradecanol	25.6	15.2	22.0
Hexadecanol	23.1	5.3	8.4
1-Ethoxy-dodecanol	19.4	10.5	15.0

wash (b), and the wet train samples (c). Each sample was analyzed separately.

Stack gas sample analysis. The samples were analyzed for sulfate level by amperometric titration and phosphate level by elemental phosphorus analysis. The organic ingredients were extracted from the aqueous solutions with methylene chloride and identified by gas chromatography-mass spectroscopy (GC-MS) using a Finnigan 4023 GC-MS unit equipped with a 25-m, silicone-coated fused silica column. The organic compounds were then quantified by gas chromatography.

The plume opacity ratings given were obtained by several observers. Each observer had been certified by the appropriate local agency by the standard EPA procedure.

RESULTS AND DISCUSSION

Total spray tower emissions. Sodium sulfate (54.2 wt%) and "volatile" organic materials (41.3 wt%) were identified as the two major components in the exhaust air stream (Table 3). Only minor levels of sodium tripolyphosphate and alcohol ethoxylate were detected despite the presence of significant quantities in the crutcher slurry.

The sodium sulfate must have originated from particulate matter passing through the collection system. The high level of sodium sulfate relative to sodium tripolyphosphate indicates some type of stratification in the system and is a direct result of the heterogeneous nature of the crutcher slurry. The high level of sodium sulfate could be a result of slow hydration rate or smaller initial particle size.

The composition of the organic material is of particular interest. It must originate from the alcohol ethoxylate by one of three routes: (i) decomposition and volatilization of the alcohol ethoxylate; (ii) particulate carryover, or (iii) volatilization of components originally present in the alcohol ethoxylate. The organic fraction was found exclusively in the wet train collection system, and only minimal levels of other inorganics were present. The organic fraction was composed mainly of linear primary alcohols and 1-ethoxy-dodecanol, 62.9 wt% (Table 4). Therefore, it could not have originated from particulate carryover, because the beginning nonionic contained only 1.85 wt% of these materials.

The presence of all identified organic components (90.8 wt%) could be explained by volatilization of components originally present in the nonionic. The ratio of alcohols present closely matched the predicted ratio calculated according to Raoult's law of partial pressures (Table 5) and was clearly different from the initial ratio present in the starting nonionic. The paraffins detected in the organic fraction originate from the alcohol used in preparing the ethoxylate and not from decomposition. The total calculated organic particulate loading (58 mg/m^3) from this sampling compared very well with the typical extractable organic from the wet train system observed in previous stack sampling. No obvious products related to decomposition (thermal or oxidative) of the nonionic were detected. Therefore, the organic components must originate from volatilization of low molecular weight compounds or exclusive decomposition of the nonionic to free alcohol. The latter selective decomposition pathway seems unlikely, and actual plant experience, to be discussed later, favors the volatilization theory.

SPRAY TOWER EMISSION COMPOSITION VERSUS PLUME OPACITY

The relationship between plume opacity and particulate loading has been developed by Pilat and Ensor [Equation 1] (6).

The basic conclusion of this work was that particle sizes in the same range as the wavelength of light have the greatest effect on opacity for a given particulate loading. As the particle size increases above the wavelength of light, the plume opacity decreases exponentially for a given particulate loading. The effect is caused mainly by the relationship between total surface area (or cross-sectional surface area) and the particle size.

$$\ln I/I_0 = -\frac{WL}{Kd} \qquad [1]$$

Opacity = 100 − ($I/I_0 \times 100$)
W = particulate loading, g/m^3
L = stack diameter, m
d = particle density, g/cm^3
K = specific particulate volume divided by the extinction coefficient, cm^3/m^2

The K term derived by Pilat and Ensor is dependent on particle size and distribution and the refractive index of the particle.

The two major components (sodium sulfate and volatile organic matter) of the materials in the exit gas stream have drastically different particle sizes based on where they were found in the EPA Method No. 5 sampling system.

The sodium sulfate was deposited almost exclusively (95+%) in the probe tube with only 2% on the glass filter and less than 3% in the wet train. Based on the distribution pattern and the work by Elder, Tillery and Ettinger (7), the particle size of the sodium sulfate can be estimated to be around 14 μm, or at least greater than 10 μm. Assuming the sodium sulfate particle behaves as a light absorber, the K value would be estimated at 1.7 to 7.0. The opacity attributed to the sodium sulfate based on the Pilat and Ensor equation is negligible—1 to 4% on 100% opacity scale. (The stack diameter is 1.22 m, and density 1.464 g/cm^3 for sodium sulfate or 0.8 g/cm^3 for the organic components.)

The organic component was trapped exclusively in the wet train and must have passed through the Reeve Angel glass filter. The organic component must have had a particle size less than one micron, or it would have been trapped mainly on the glass filter (8). It is quite likely that the organic components were actually in the vapor phase in the sampling apparatus. The organic vapor was thus trapped only by the Greenburg-Smith impingers in the wet train.

The particle size of interest is the particle size at the point of opacity reading. For a spray drying operation, the generally accepted monitoring point is where the steam plume has revaporized or directly above the stack under low humidity conditions. For the sodium sulfate, the estimated particle size is appropriate, because the particle size will not decrease from the sampling point. However, we do not have a measurement of the particle size of the organic components at the monitoring point. The vapor should spontaneously condense upon contact with the much cooler ambient air. If we assume the worse case, particle size between 0.4 and 0.8 microns (wavelength of visible light), the K value would be 0.15 to 0.3. The opacity attributed to the organic component would then be between 27 and 46% (100% scale) (7). The observed opacity during the stack sampling experiment was 45 to 50%. Therefore, our original assumption concerning particle size appears validated. Thus, the observed plume opacity can be attributed almost entirely to the organic component of the particulate loading in the exit gas. The organic component is exclusively trapped in the wet train. Therefore, the wet train particulate loading should be directly related to observed plume opacity. The results of subsequent plant trials, as shown in Table 6, support this theory because a good correlation is noted with wet train particulate loading and not with the dry train particulate loading.

TABLE 6

Plume Opacity Versus Particulate Loading

Identity	Particulate loading[a] (mg/m^3) Dry train	Wet train[b]	Plume opacity (%) Predicted[c]	Observed
Stack sample run	75.9	58.2	27-46	45-50
Control Nonionic No. 1	72.8	20.3	10-18	5-10
Control Nonionic No. 2	115.5	34.3	13-24	10-15
Control Nonionic No. 3	48.0	62.8	27-47	40-45
14-12, 70 (peaked), No. 1	39.7	20.3	10-19	20-25
14-12, 70 (peaked), No. 2	20.9	5.8	3-6	5-10
14-12, 70 (peaked), No. 3[d]	67.1	18.7	9-17	5-10
14-12, 70 (peaked), No. 4[d]	121.9	26.6	10-19	5-10

[a] EPA Method No. 5 sampling system.

[b] Extractable organics.

[c] Opacity predicted from the Pilat-Ensor equation using a K value of 0.15 to 0.3 and assuming only the wet train contributed to pluming.

[d] High spray tower loadings.

Plant trials. The plume observed during the spray drying of a nonionic-based powdered detergent has been attributed to the organic materials in the exhaust. The organic loading must occur by either volatilization or selective decomposition to alcohols. A close examination of several results from plant trials of various nonionics will allow us to differentiate between these two possibilities.

An alcohol ethoxylate of similar composition to that used for the stack sampling experiment caused extensive pluming problems, even when diluted with standard material. The free alcohol level of this material was found to be 2.82 wt% (versus 1.54 wt%) with a significant level of decanol (0.16 wt%). In another case, an alcohol ethoxylate with the same alcohol composition and degree of ethoxylate was produced using the technology (4) to peak the ethylene oxide homolog distribution. The free alcohol level of this material was 0.4 wt% versus standard of 1.54 wt%. The plant trial of this material resulted in a substantially reduced plume opacity, 20%, versus 45 to 50% observed during the stack sampling test.

In both of these instances, the alcohol base and degree of ethoxylation were not altered. The only significant change was in the amount of free alcohol. If selective decomposition to alcohols was the predominant mechanism responsible for the organic loading, no change in plume opacity would have been predicted. However, if simple volatilization of free alcohols was the predominant mechanism responsible for the organic loading, the observed plume opacities would match the prediction exactly. Therefore, volatilization and recondensation of low molecular weight compounds (mainly free alcohols) has been shown to be the predominant mechanism responsible for organic loading and the resultant plume opacity.

Choosing a nonionic for spray drying. The plume opacity has been shown to be directly related to the low molecular weight components (mainly free alcohols) in an alcohol ethoxylate. The amount of material in the vapor phase will be a direct function of the quantity of material present and its volatility. The amount of free alcohol and one-mol ethylene oxide adduct is inversely related to the degree of ethoxylation. Therefore, an alcohol ethoxylate with the highest practical level of ethylene oxide should be used to minimize pluming problems. The volatility of the free alcohols will depend exclusively on their molecular weight. In order to minimize volatility, an alcohol with the highest molecular weight should be used to minimize pluming problems.

However, the alcohol ethoxylate chosen for a spray drying application must perform its intended purpose as a surfactant in addition to processing considerations. Unfortunately, the optimum performance is often obtained at lower ethoxylation levels and lower alcohol molecular weights. Therefore, a compromise between performance and processing considerations must be reached.

A new ethoxylation catalyst was developed recently which peaks the distribution of ethylene oxide adducts and reduces the free alcohol by 60% for a given ethoxylation level (4). The use of these ethoxylates expands the options of the formulator to utilize a lower degree of ethoxylation or lower alcohol molecular weight with pluming characteristics equivalent to those of a conventional product. The development of Novel™ 1412-70 alcohol ethoxylate was based on this technology. Plant trials at three separate locations (Table 6) demonstrated both the reduced pluming tendency of this material and also the feasibility of increasing the spray tower throughput while complying with air quality regulations; subsequent commercialization has been successfully completed.

The qualitative concepts for choosing a nonionic have been outlined. However, a quantitative tool would be of value. The physical property of interest is the vapor pressure of the nonionic at typical spray drying conditions. For convenience, the vapor pressure at 149 C will be examined. Ideally, the vapor pressure of the nonionic in question should be measured. However, the vapor pressure of suitable nonionics at this temperature is less than 1 torr. It is difficult to obtain accurate experimental data under these conditions. An alternative to direct measurement would be to calculate the theoretical vapor pressure using Raoult's law of partial pressures. In order to calculate the vapor pressure, we need to know the vapor pressure of the pure components at 149 C and the quantity of each component present. The vapor pressure of the free alcohols and ethoxy derivatives are readily obtained from the open literature (Table 7) (9,10). The quantity of each component can be determined readily by GLPC analysis. The relative vapor pressures at 149 C for several nonionics are shown in Table 8 along with the plume opacity observed during actual plant trials. The observed correlation provides additional support to the theory that pluming is caused by volatilization and recondensation of low molecular weight components in an alcohol ethoxylate. Therefore, an estimate of the relative pluming tendency of alcohol ethoxylates can be obtained by calculating their vapor pressure at 149 C.

Another quantitative method for selection of a nonionic for spray drying is the smoke point (11) of the nonionic. The smoke point, which is the temperature at which a heated sample emits a thin, continuous stream of smoke, was measured for several nonionics (Table 8). The smoke

TABLE 7

Relative Vapor Pressures of Pure Compounds at 149 C

Compound	Vapor pressure (Torr, 149 C)	Reference
Decanol	51.9	9
Dodecanol	16.2	9
Tetradecanol	4.8	9
Hexadecanol	1.9	9
1-Ethoxydodecanol	4.6	10
1-Diethoxydodecanol	1.0	10
1-Ethoxytetradecanol	1.9	10

TABLE 8

Alcohol Ethoxylate Vapor Pressures Versus Plume Opacity

Identity[a]	Vapor pressure at 149 C (Torr × 10^2)	Smoke point, °C	Plume opacity
12-18, 70[b]	47.5	141	45-50
12-18, 70 (peaked)[c]	6.1	160	20
12-18, 70 (high decanol)[d]	124.3	129	Excessive 60+
14-12, 70 (peaked)[e]	6.6	161	15-20
Alternative nonionic	10.0	153	30

[a] The first 4 numbers relate the carbon chain length; *12-18*, 70, dodecanol to octadecanol. The second number is the approximate weight percent ethylene oxide; 12-18, *70*, 70 weight percent ethylene oxide.

[b] Stack sample test.

[c] Plant trial on material produced via peaked ethoxylation catalyst.

[d] Plant trial of problem material containing a high level of decanol.

[e] Commercial low-pluming nonionic.

point temperatures have been proven both to be indicative of the intensity of the spray tower exhaust opacity and to be suitable for a quality control criterion for assessing the acceptability of individual nonionic raw material receipts.

The smoke point test can be viewed as a visual vapor pressure test. The thin, continuous stream of smoke is a direct result of a constant quantity of material vaporizing and recondensing. The temperature at which this occurs is directly related to the vapor pressure of a particular nonionic. The relationship between the smoke point temperature and vapor pressure is defined by the Clausius-Clapeyron equation.

The effect of paraffin impurities in the starting alcohol has not been addressed. Although present at very low levels in the final alcohol ethoxylate, they do contribute to the observed plume. The paraffin composition will reflect the alcohol composition. The contribution to pluming will be reduced by increased ethoxylation level as a result of simple dilution. The effect of free alcohol is the major item affecting organic loading in current operations and the one which can be most readily controlled. Therefore, the effect of paraffin impurities has been set aside for this discussion.

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♣Changes in Physico-Chemical Properties During Decomposition of Nonionic Surfactant Solutions

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The decomposition and accompanying changes in surface chemical properties of nonionic surfactants were investigated. The decomposition of nonionic surfactants occurs in the polyoxyethylene and ester chains. Ester chains were susceptible to decomposition with an increase in the polyoxyethylene chain length, but polyoxyethylene chains were not. Surface chemical properties such as solubilizing power, surface tension, effective specific volume, and intrinsic viscosity also deteriorated during decomposition of the surfactants.

Knowledge of surfactant decomposition is of fundamental importance in understanding the stability of solubilizates. We have reported previously that the oxidation stability of benzaldehyde derivatives in aqueous solutions of nonionic surfactants is affected by micellar structure (1,2). Hamburger et al. (3) also found that surfactant decomposition has a pronounced effect on the stability of solubilizates. Surfactant decomposition, including biodegradation as well as chemical decomposition, has been studied extensively (4-6). However, nonionic surfactant decomposition still is not clearly understood (7,8).

In this paper, we report on the decomposition and accompanying changes in surface chemical properties of nonionic surfactants in solution.

EXPERIMENTAL

Materials. Polyoxyethylene monostearates (PMS-n, n = 25, 45, 55, where n is the average number of ethyleneoxide groups) were obtained from Nikko Chemicals Co. Ltd. These nonionic surfactants were purified by extraction (1). Other reagents were extra pure grade and were used without further purification. Only double-distilled ion-exchanged water was used.

Methods. Surfactant solutions (15 ml, 5×10^{-3} M) were kept in 30 ml corked glass tubes at 40 ± 0.1 C. The surfactant concentrations were well above their cmc (2).

The cloud point was determined by heating a solution containing NaCl (1 M) in a test tube and recording the temperature at which the solution became turbid. The NaCl lowered the cloud point to below the boiling point (3).

Peroxides were determined by the iodometric spectrophotometric method of Azaz et al. (9).

Conductivity and pH were measured using a conductivity meter (Takemura Electric Works Ltd., Model DM-37) or a pH-meter (Central Kagaku Co., Model HG-3), respectively. Turbidity was measured using a turbidimeter with an integrating sphere (Nihon Seimitsu Kogaku Co. Ltd., Model SEP-H). The degree of the turbidity was calculated using the following formula:

$$\text{Turbidity}\ (\%) = \text{Td}/\text{Tt} \times 100$$

where Td is diffused transmittance and Tt is total transmittance.

Stability of ester chains was determined by the method of Samejima et al. (10).

The solubilizing power of PMS-n was determined in terms of solubility of Orange OT by the method of Al-Saden et al. (11). Surface tension measurement was made using a Wilhelmy plate and torsion balance (Kyowa

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