Vitamin Product Forms and Stability and Retention Through Processing and Storage

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Introduction

Suppliers face the daunting task of producing vitamins so that losses during storage and feed processing are minimized. Simultaneously, bioavailability and mixing characteristics must be maximized – all in a cost-effective manner, of course – for a product added to feeds in very small amounts.

No product form can assure complete and unlimited stability of a vitamin. However, the more advanced product forms available to commercial feed and premix manufacturers provide stability far superior to the raw vitamin product (Kurnick et al., 1978).

And product forms improve over time. The primary vitamins of concern for stability were vitamins A and D, menadione, thiamin and vitamin C in the late 1980s (Gadiet, 1986). Today, we can probably remove vitamins A, D and C from that list due to improved product formulations – at least for most feed processing conditions.

But not all vitamin products are created equally. Differences in company-exclusive technology prevent us from making wholesale statements across vitamins, since vitamin stabilities are associated with specific manufacturers.

Product development is a complicated process. Bioavailability and uniform vitamin activity within the product form, and optimal handling and mixing characteristics must be considered (Frye, 1994). Good flowability, low dustiness, low hygroscopicity and caking, and minimal segregation and carryover effects are essential components.

Lastly, new sources of vitamins in the feed industry require confirmation of efficacy and stability. Certainly, as feed manufacturers shift to more aggressive processing methods, vitamin stability should be periodically revaluated.

Not All Vitamins Are Equal in Stability

Commercial vitamins for feeds and foods are formulated to counter anticipated stresses, and these formulations act as a buffer between the vitamin and the aggressor. Differences exist in the stability of vitamins in their natural form (Baker, 1995). The ability of vitamins to withstand the rigors of storage in mineral premixes (Shurson et al., 1996) or in the presence of choline chloride is not good (Tavacr-Kalcher and Vengust, 2007).

The primary considerations for vitamin stability are listed in **Table 1**, and include heat, moisture, light and pH. As noted, the stability characteristics differ across a variety of conditions for the full collective of important vitamins. It is the unique chemical structure and other characteristics of each vitamin that directs the type of stabilization or formulation.

For example, heat can be especially destructive to vitamin A, folic acid, or vitamin B_{12}, yet has little consequence on niacin or riboflavin. Therefore, the focus on some vitamins is to lessen their weaknesses to heat, knowing that most feed processing methods utilize heat.

Another example would be vitamin A with four double bonds and one hydroxyl group (Adams, 1978). This chemistry predisposes vitamin A to oxidation, thus esters of vitamin A (actetate, palmitate, and propionate) help avoid oxidative destruction. Along with beadlet formation, this provides protection against moisture and light, and improves handling abilities.

Tocopherols have special anti-oxidative capabilities through the free phenolic hydroxy group, and this seriously compromises the stability of vitamin E in the alcohol form. Esterification with acetic acid eliminates the anti-oxidative nature, thereby improving stability for premixes and feeds.

Vitamin K (ie, menadione) is one of the more unstable vitamins due to its structure, but modifications improve stability characteristics. Thiamin and folic acid are prone to bind with the carbonyl group of reducing sugars through the Maillard reaction (Baker, 1995), and higher pelleting temperatures increase this occurrence. In crystalline form, some vitamins require no special protection. Ca-pantothenate, niacin and niacinamide (nicotinamide) exhibit excellent stability characteristics for pelleting, thus changes here are directed for other purposes.

In the end, the inherent chemical and stability characteristics, along with intended commercial application, largely direct vitamin formulations to help offset shortfalls. Improvements beyond stability dwell on handling characteristics (ie, hygroscopicity, dustiness, flowability) and aesthetic considerations.

Formulation of Vitamins

The basic chemical forms of vitamins are formulated uniquely to avoid some of the most obvious stresses and negate inherent weaknesses (**Table 2**). Two basic technologies are generally utilized.

Chemical modification works for vitamin A, E and C, in that the reactive hydroxyl groups are protected by esterification. Antioxidants may also be included for added protection. Ultimately, chemical changes must not interfere with bioavailability and other essential objectives.

Physical protection is applied in various formulations to develop a barrier to protect against oxygen, moisture or light. Often, the formulation will differ across manufacturers and formulation technologies due to patents and proprietary techniques, hence not all will equally protect against degradation. A 20% improvement existed for the Rovimix®[1] form across four different sources of vitamin A beadlet pelleted at 194°F (DSM Internal VFP9964).

Vitamin A protection is a good example of both technologies being utilized with one vitamin. Once chemically stabilized, further improvements are made by cross-linking with gelatin in a 'beadlet'. Fructose and glycerine enhance the process to ensure protection against moisture and heat during feed manufacture. The protein-based coating is then hydrolyzed by intestinal proteases, thus releasing the vitamin A for absorption.

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[1] Rovimix is a registered trademark for DSM Nutritional Products

Feed Processing

Pelleting. Conditioning/pelleting temperature is the most obvious contributor to vitamin losses for poultry and swine feed. According to Van't Hoff's Rule, an increase in temperature by 10°C will increase the rate of chemical reactions by 2- to 3-fold. Thus, during conditioning of feeds, the integrity of the vitamin is threatened with exposure to oxygen and trace minerals when the coatings of some beadlet or spray dry forms are softened and disintegrate.

And once the beadlet or some aspect associated with stability is damaged during the conditioning process, this vitamin becomes more exposed and more prone to continued damage in the pelleted feed. Thus, loss in activity in pelleted feed is not limited to the feed as it exits the pellet die.

Conditioning time affects vitamin degradation, with a longer conditioning time posing the greater threat. The goal of conditioning feed is to uniformly penetrate each feed particle with moisture and heat. Under pressure and with rigorous mixing in the feed conditioner, this creates an environment especially harsh to vitamins and other feed additives.

Often, moisture is increased to 17-18%, and provides a solvent for destructive agents since moisture is often essential for harmful chemical reactions.

The type of feed, mineral and fat content must be considered. Each brings characteristics that can influence the degree of friction as the feed passes through the die. At least theoretically, we expect lower vitamin degradation in finisher type diets (ie higher fat, lower mineral content). The addition of high meat & bone meal, along with increased corn DDGS in feeds, can increase the friction through the die. We are currently investigating this aspect to determine if such feed character can result in meaningful changes in survival through the die.

Ultimately, vitamin survival through feed processing is a multi-factorial process. Changes in conditioning time, fat level, old versus new corn, etc., conceivably could change survival. Thus, in the end, factors other than pelleting temperature by itself must be considered.

Expanders. Annular gap feed expanders encompass a rapid pressure build-up with an increase in temperature to approximately 220-230°F for 3-5 seconds. At the outlet, both temperature and pressure decline rapidly, and moisture is quickly lost. The conditioning temperature is also a factor, which could be 180-190°F. Although the high temperature and pressure threaten vitamin stability, the time period is very short. Expander results from stability studies for feed additives tend to be mixed.

Extrusion. The extrusion process can be rigorous with high heat and steam pressure over a longer time period than for pelleting or expanders. Thus, compared to pelleted feeds, vitamins in extruded feeds generally have a lower retention or survivability. Moisture can be as high as 35-40%, or twice as high as conditioning during pelleting. As with pelleting, longer conditioning times, higher moisture and higher temperatures offer the greatest threat.

In a nice review on extrusion and vitamin stability, Texas A & M researchers (Riaz et al., 2009) note that barrel temperature, screw rpm, moisture, and die diameter contribute to vitamin survival in the final feed. Generally, across a number of trials and conditions, vitamins A, E and C, along with folic acid and thiamin, were most sensitive to extrusion.

Vitamin Stability

Based on a number of studies, the expected retention or stability of the various commercial vitamins in feeds pelleted at 170 to 200°F is noted in **Table 3**. Above 200°F, or under unusual conditions of extended conditioning times or double pass conditioners, estimates should be pressured downward to account for additional losses. An analysis of the feed might needed.

Recently, we completed a pelleting vitamin stability trial at Kansas State University to test Rovimix® vitamins at a relatively low pelleting conditions (160°F/30 sec) versus one designed to be more harsh (190°F/60 sec; **Table 4**). Difference in losses was not large between the two sets of conditions. With the exception of vitamin A, at the higher temperature and conditioning time, recovery was close to 90% or greater.

Vitamins need this type buffer. Pelleting temperature can be low at the initiation of feed production early in the day and then increase to higher target temperatures as the equipment reaches a high production rate. Summer versus winter, old corn versus new corn, as well as other factors, can change pelleting temperatures within a given time. Thus, vitamin manufacture attempts to stabilize survival rates over a range of conditions to lower variability in feeds.

In a recent field study, the stability of vitamin A, vitamin E adsorbate, riboflavin, thiamin and folic acid was determined when the feed was conditioned for 3 minutes at 205 to 210°F, and in a cooker for 5 seconds at 240°F. Losses of were minimal, being 10% for vitamin A, riboflavin and folic acid (**Table 5**). While no loss occurred with thiamin, 25% of the vitamin E was lost. Under relatively harsh conditions, stabilities were generally good overall.

Post-processing Vitamin Losses

Mentioned earlier, during feed processing the protective coatings can be damaged such that intimate contact with solubilized trace elements and moisture becomes a greater possibility. While the majority of poultry and swine feeds is consumed within days after pelleting, bagged pelleted feeds might be stored for several weeks or months.

In such cases, considerations must be made for the time lag between pelleting and feeding, since a potency loss can continue with prolonged storage. Additional levels in the feed can offset higher anticipated losses.

Altemueller and Gadient (2008) reviewed several groups of data and provide anticipated losses of vitamins in feeds that were pelleted, or expanded or extruded, and then stored for 3 months at 77°F **(Table 6)**. The extruded feed is expected to suffer the greatest loss over the ensuing 3-month period.

In a recent study to compare commercial sources of vitamin A for a 3-month period after mixing in a premix, and then another 3 months after adding to animal feed (Altemueller and Gadient, 2008). The biggest loss (30%) occurred early during the 'premix phase' with two of the three commercial vitamins. The Rovimix Vitamin A 1000 suffered only marginal losses. Such data are important to feed manufacturers that prepare complete feeds.

Gadient and Fenster (1992) reported a loss of 20-30% for most vitamins when stored three months at 95°F after being pelleted at 194°F. Losses in vitamins due to various storage conditions have been reported (Kurnick et al., 1978; Anonymous, 1991; Albers, 1996). At room temperature for 8 weeks after pelleting, thiamin, menadione, pantothenic acid, folic acid and vitamin B12 appeared most prone to losses (Albers, 1996).

Little information exists in the literature regarding the effect that other additives might have on vitamin stability during pelleting. Hooge et al. (2000) reported that the stability of vitamin A, vitamin E and riboflavin improved in the presence of tribasic copper chloride in a broiler starter feed. No pelleting temperature or conditioning time was given.

Vitamin Losses in Premixes

A number of studies find vitamins to lose activity in the presence of inorganic trace minerals, especially when choline chloride is present. University of Minnesota's Shurson et al. (1996) completed a trial that compared stabilities in 4 treatments:

1. Pure vitamin alone
2. Premix with only vitamins
3. Premix with inorganic trace minerals
4. Premix with amino acid mineral complexes

Over a 120-day period with a temperature of about 87°F, the most resistant vitamins were Ca pantothenate, vitamin E, riboflavin, biotin and niacin. Those experiencing the greatest losses were vitamin A, vitamin K, pyridoxine and thiamin. Over all treatments, vitamin loss was greatest in the inorganic trace mineral premix. Based on the results, vitamins were ranked as a low-cost assay stability indicator for quality control purposes. Vitamin A was deemed best indicator, and then thiamin, vitamin K and vitamin B12 (Shurson et al., 1996).

Ultimately, losses can be reduced 40-50% by storing vitamins and trace minerals separately until added to feeds (Shurson et al., 1996). Amino acid-specific trace mineral complexes provide additional advantage, as opposed to inorganic trace minerals, for lowering vitamin losses.

Tavacr-Kalcher and Vengust (2007) found choline chloride to increase vitamin destruction in premixes void of trace minerals. Over a 12-month period, the concentration of vitamins A, D and K decreased to 53, 59 and 80% of the original content. In the presence of choline chloride in the premix, these values declined to 39, 50 and 9% of their initial levels. No other vitamins were analyzed.

Table 7 provides general recommendations for vitamin stabilities when stored alone or in a premix containing choline chloride and trace minerals. Caution must be exerted since temperature and humidity, and vitamin source, will heavily impact expectations in vitamin losses.

Other Feed Additives

25-OH vitamin D_3. For pelleting, 25-OH vitamin D_3 shows good stability, in spite of the presence of a free hydroxyl. The commercial form of this product (25-OH vitamin D_3, HyD®) is prepared in beadlet form using proprietary technology. In one trial, stability at 158 and 194°F was 95 and 85%, respectively, of the amount added in the mash feed. In another study, survival through pelleting was 90% or better at pelleting temperatures of 158 to 185°F, but was 78% at 194°F. Thus, it appears that a loss of about 15% occurs at about 194°F, and possibly more at higher pelleting temperatures.

Conclusions

The stability of vitamins for feed processing continues to improve. Most vitamins exhibit good stability (90 to 100% at 180°F), although other factors influence survivability. Product formulations differ and differences exist in survivability across commercial formulations. Additional supplementation rates are often employed to compensate for pelleting losses. Vitamins can be destabilized in premixes with inorganic trace minerals, and the losses can be increased when choline chloride is present.

Along with survival determinations for vitamins at the pellet die, consideration is needed for a time lag of several weeks or more between manufacture and consumption of that feed.

Table 1. Factors Affecting the Inherent Stability of Vitamins (nonformulated forms)

Vitamin	Heat	Oxygen	Water	Light	Acid	Alkali
A	XX	XX	X	XX	X	O
D_3	X	XX	X	X	X	O
E	X	O	X	X	O	X
K (menadione)	X	X	XX	O	XX	O
Thiamin	X	X	XX	O	O	XX
Riboflavin	O	O	X	XX	O	O
Pyridoxine	XX	O	X	X	X	O
Vitamin B_{12}	XX	X	X	X	O	O
Ca Pantothenate	X	O	X	O	X	O
Niacin	O	O	O	O	O	O
Folic acid	XX	O	XX	XX	XX	O
Biotin	X	O	O	X	O	O
Vitamin C	O	XX	XX	O	O	X

O = stable, X = sensitive, XX = very sensitive

Table 2. Common Commercial Vitamin Forms

Vitamin	Commercial Formulation	Rationale
Vitamin A	Ester in a cross-linked beadlet	Stability
Vitamin D_3	Spray dry	Stability, uniform distribution
Vitamin E	Acetate ester granular or spray dry	Stability, flow, reduced dustiness
Vitamin K (menadione)	Crystalline powder	Flow, handling
Thiamin	Coarse granular	Stability
Riboflavin	Spray dry granular	Stability, flow, handling
Pyridoxine	Fine granular crystalline	Stability, mixing
Vitamin B_{12}	Crystalline with carrier	Distribution
Niacin	Crystalline	Flow, reduced dustiness
Niacinamide	Crystalline	Flow, reduced dustiness
Ca-Pantothenate	Spray dry	Flow, reduced dustiness
Biotin	Spray dry	Distribution, handling
Folic Acid	Spray dry	Flow, stability, mixing
Vitamin C	Ethyl cellulose coated	Stability
Vitamin C phosphorylated	Phosphorylated	Best stability; biopotency

Table 3. Range in Estimated Stability of Vitamin Products at Different Pelleting Temperatures

Vitamin	170 F	180 F	190 F	200 F
A beadlet	90 - 100	90 - 100	90 - 95	85 - 90
D_3 beadlet	90 - 100	90 - 100	90 - 95	85 - 90
E actetate	90 - 100	90 - 100	90 - 95	80 - 90
E spray dry	90 - 100	90 - 100	90 - 95	85 - 90
K (menadione sodium bisulphite)	50 - 60	40 - 50	40 - 50	35 - 40
K (menadione nicotinamide bisulphate)	80-90	70-80	65 - 75	65-75
Thiamin monohydrate	90-100	90-100	90-95	85-90
Thiamin HCl	90-100	85-95	85-95	70-80
Riboflavin	90-100	90-100	90-95	85-90
Pyridoxine	90-100	90-100	90-95	80-90
Vitamin B_{12}	90-100	80-90	70-85	60-80
Ca Pantothenate	90-100	90-100	90-95	85-90
Niacin	90-100	90-100	90-95	85-90
Niacinamide	90-100	90-100	90-95	85-90
Folic acid	90-100	85-90	80-90	70-80
Biotin	90-100	90-100	90-95	85-90
Vitamin C ethylcell.	50-80	40-70	30-60	20-40
Vitamin C phosphorylated	90-100	90-100	90-95	90-95

Based on 30 to 45 second conditioning time

Table 4. Summary of Vitamin Retention (%) at Two Pelleting Temperatures and Conditioning Times

Temperature, °F	160	190
Conditioning time, sec	**30**	**60**
Vitamin A (A/D_3)	85	84
Vitamin D_3 (A/D_3)	98	90
Vitamin D-500	91	81
Vitamin E Adsorbate	88	89
Vitamin E spray dry	85	87
Riboflavin-80	100	100
Rovimix Pyridoxine	98	102
Rovimix Ca Pantothenate	90	95
Rovimix Biotin	100	100

Table 5. Vitamin Stability in High Pressure Feed Processor

Feed	Vitamin A, IU/lb	Vitamin E, IU/lb	Riboflavin, mg/lb	Thiamin, g/lb	Folic Acid, mg/lb
Mash	3768	12.85	3.39	2.46	400
Feed	3367	9.58	3.10	2.53	370
% Recovery	89	75	91	103	92

Table 6. Retention of Vitamins in Feed Processed and Stored at 77°F for 3 Months

	Pelleting	Expander	Extrusion
	% Retention		
Vitamin A	85-95	70-90	70-90
Vitamin D_3	90-100	80-100	75-100
Vitamin E	90-100	90-100	90-100
Vitamin K (menadione)	70-90	30-50	20-50
Thiamin	70-90	50-70	60-80
Riboflavin	90-100	90-100	90-100
Pyridoxine	90-100	80-90	80-90
Vitamin B_{12}	90-100	50-80	40-80
Ca-pantothenate	95-100	90-100	90-100
Niacin	90-100	90-100	90-100
Folic	70-90	50-70	50-65
Biotin	90-100	90-100	90-100
Vitamin C	80-100	80-100	80-100

Altemueller and Gadient, 2008

Table 7. Retention (%) Expectations of Vitamins in Premixes Stored 3 Months

Vitamin	Vitamins Only	Vitamins, minerals, and choline chloride
Vitamin A	90-100	70-90
Vitamin D	90-100	80-100
Vitamin E	90-100	90-100
Vitamin K	50-70	30-50
Thiamin	85-100	70-80
Riboflavin	90-100	90-100
Pyridoxine	70-90	60-80
Vitamin B_{12}	60-90	50-80
Pantothenic acid	90-100	80-100
Niacin	90-100	90-100
Folic acid	70-90	50-70
Biotin	90-100	70-90
Vitamin C	90-100	90-100