THE USE OF FLY ASH IN THE MANUFACTURE OF ASPHALT SHINGLES

DONALD E. SHAW
JTM Industries, Inc.
Kennesaw, Georgia

Mineral stabilizer, or filler, is a major raw material requirement in the manufacture of the majority of prepared asphalt roofing products, such as shingles. This paper discusses the potential advantages of using fly ash, which is produced as a by-product from the burning of coal for the generation of electricity. Careful selection and processing of fly ash sources can lead to the production of a filler material that is technically and economically viable for the shingle market. From 1992 through the end of 1996, more than 544,680 metric tons (600,000 tons) of fly ash were used in the manufacture of roofing shingles. The fly ash properties of note include a relatively inert surface reactivity, very low oil absorption, spherical particle morphology, relatively low specific heat, and an opacity to ultraviolet light. Laboratory testing that favors suitable fly ash over traditional fillers include markedly superior performance in laboratory-simulated weathering/UV exposure studies and a lower compound viscosity. This lower viscosity results in a lower energy requirement in the shingle manufacturing process. Empirical observations from the field give strong indications that fly-ash-filled shingles are resistant to algae growth/discoloration.

KEYWORDS

Coating asphalt, filler, fly ash, limestone, shingles, weathering.

SHINGLE MANUFACTURE

Each year, the roofing industry produces well over 929 million m^2 (100 million squares) of asphalt shingles.[1] There are different types and styles of these shingles, and mineral stabilizer (filler) is a major component of all of them. In fiberglass-mat-based shingle manufacture, filler composes approximately 40 percent of the total finished product weight. A reasonable estimate of the total annual filler requirement for shingle manufacturing in the United States would be in excess of 5 million tons (4,539,000 metric tons).

Over the past several decades, many different types of pulverized and/or finely divided mineral matter have been utilized as filler in the manufacture of shingles. Today, both dolomitic and high-purity limestone have the dominant market share in those manufacturing plants where naturally occurring minerals are used. Exceptions include those situations where freight sensitivity or other economic restrictions make the use of alternate materials necessary and those locations that have deliberately switched to fly ash filler because of the perceived enhancements to the manufacturing process and the finished product. As of this writing, fly ash composed approximately 10 percent of the shingle filler market.

In order to understand the opportunity for fly ash to penetrate this market, it is first necessary to understand the fitness-for-use requirements for filler in prepared roofing products, the reasons why limestone has been commonly specified, and the relevant properties of fly ash.

FILLER REQUIREMENTS

A list of idealized filler characteristics for the manufacture of shingles relates to the effects that result from compounding the filler with coating asphalt in the manufacturing process and the subsequent service requirements on a roof. Such a list would include the following:

■ *Economical*—In order for any product to be considered, an economic value must be demonstrated.

■ *Environmentally benign*—Environmental concerns are vital in all businesses. Relevant concerns specific to roofing manufacture include airborne dust during the manufacturing process and toxic leaching potential of individual raw materials and consequently, the finished product.

■ *Low free lime content*—A common specification among shingle manufacturers is a limit on the free lime (CaO) content in filler. Roofing industry experience has shown that an excess amount of lime can react with certain asphalt constituents to greatly accelerate granule loss from the shingle, resulting in premature failure of the roof.

■ *Capable of producing low compound viscosities*—Shingle manufacturers specify and measure filler usage as a weight percent of the asphalt/filler mixture. In order to be economically viable, a filler must be able to provide a workable viscosity (<4,000 centipoise) at a 65 percent (weight filler) loading during the manufacturing process. Further, because asphalt viscosities are temperature-dependent, the advantage lies with the filler whose compound viscosities are relatively lower than another candidate filler.

■ *Stabilization of coating asphalt*—One of the primary reasons for filler usage is to increase the stability, or flow resistance, of the coating asphalt. Given shingle surface temperatures that can approach 100°C (212°F),[2] unfilled asphalt would have to be very highly oxidized to resist flowing down the roof slope. Such a high state of oxidation would result in brittleness and a dramatically reduced ability to perform throughout the roof's expected service life.

■ *Nonabsorptive (porous) particles*—Some filler particles will absorb the light oil component of asphalt. Although this may provide improved mechanical strength upon initial evaluation, the lighter asphalt fractions are important in extending ductility and pliability over time.

■ *Opaque to UV radiation*—It has been established that UV radiation accelerates the degradation of asphalt by catalyzing the formation of water-soluble free radicals.[3]

■ *Little or no calcium carbonate (CaCO₃) content*—After three to five years of exposure, especially in warm, humid climates, many roofs start to exhibit a dark, streaky discoloration. Typically referred to as fungus, it is caused by a variety of algae and bacteria. Experiments have shown that calcium carbonate may provide nutrients to catalyze this growth.[4]

■ *Relatively low specific heat*—A filler with lower specific heat results in filler heating energy savings during the asphalt/filler mixing process and also allows for more rapid cooling of the web after sheet formation prior to shingle cutting and packaging.

LIMESTONE PROPERTIES

Limestone enjoys market dominance as a roofing filler for several reasons, including:

■ It is an abundant, naturally occurring mineral; therefore, it is easy to find an acceptable source within a reasonable freight distance to the roofing manufacturing plant.

■ The roofing industry has a long history of relatively satisfactory experience with limestone-filled shingles on roofs across the nation.

■ Compared to other naturally occurring minerals, it reacts with asphalt in a relatively benign manner (i.e., it does not dramatically increase the brittleness of the shingle, nor does it promote granule loss).

■ It has a specific gravity of about 2.65. Coupled with a blocky, though irregular, particle shape, acceptable weight loadings are obtainable at the required process viscosities.

There is no question that limestone fillers can be employed to produce high-quality asphalt shingles. However, if one considers the idealized filler properties listed above with the inherent properties of typical limestone, the possibility exists that one could find a filler product with better fitness-for-use characteristics.

FLY ASH PROPERTIES

Fly ash is often considered to be an undifferentiated generic commodity, particularly by those not familiar with the coal combustion by-product industry. Accordingly, initial responses from some shingle manufacturers indicated that fly ash had been evaluated in the past and was found to be unacceptable for one reason or another. It is certainly true that there are many sources of fly ash that are totally unacceptable as an asphalt filler. To understand why, an explanation of fly ash generation from pulverized coal boiler units is necessary.

Integral to any given coal deposit are mineral inclusions. Additionally, some of the surrounding mineral matter will be collected during the coal mining process. Once received at the power plant, the coal (and accompanying mineral matter) is crushed to a particle size that is >90 percent finer than 75 microns (3 mils) in order to maximize combustion efficiency. During the combustion process, temperatures can exceed 1600°C (2912°F), sufficiently high enough to melt most of the inorganic minerals present. The surface tension

forces acting on the melt will minimize the surface free energy and thus create spherical particles. These molten ash spheres exit the combustion chamber along with the gas stream and experience a rapid temperature reduction that quenches them into a glassy solid state.[5] Collection of the fly ash particles is typically accomplished through the use of electrostatic precipitators, bag houses, or a combination thereof. For any given source of fly ash, the chemical and physical properties are influenced by the origin of the coal, crushing efficiency, boiler thermodynamics, and collection technique.[5]

Although all fly ash sources have several common properties, each is unique in certain characteristics. Some of the relevant common properties include spherical particle shape, opacity to UV light, and a nonporous, nonabsorptive particle surface. Further, when compared to limestone, fly ash has a lower specific heat. Source-specific properties include chemical analysis, true particle density distribution, particle size distribution, bulk density, and other properties that affect compound viscosity.[5, 6]

Source-specific properties are primarily influenced by the mineralogy of the fuel source. The chemical composition of any given ash is going to be essentially the same as the soil native to the area surrounding the particular fuel source (i.e., the common earth elements will predominate).[5] The data listed below is a bulk chemical analysis conventionally expressed as elemental oxides for a typical filler-grade fly ash.[6]

These elements, along with whatever others are present in trace amounts, are tightly bound in the glass matrix formed though the melt-quench process described previously. As such, they are only leachable in very strong acid environments.[5]

Identification of those fly ash sources that are suitable for the roofing market requires an in-depth understanding of how the more than 440 sources of fly ash differ from one another. An initial screen includes a measure of free lime content that is influenced by the presence or lack of calcium carbonate located in and among the fuel deposits. After eliminating from consideration those sources of fly ash with unacceptable chemistry, such as an unacceptable level of free lime or unacceptable leaching potential, economics requires an identification of those ash sources that can produce acceptable viscosities at the required weight percent loadings in asphalt coatings.

Silica, SiO₂	56.58
Alumina, Al₂O₃	20.21
Iron Oxide, Fe₂O₃	7.65
Calcium Oxide, CaO	9.20
Titania, TiO₂	1.22
Magnesium Oxide, MgO	2.47
Potassium Oxide, K₂O	1.16
Sodium Oxide, Na₂O	0.28
Sulfur Trioxide, SO₃	0.38
Phosphorous Pentoxide, P₂O₅	0.21
Manganese Oxide, MnO	0.18

Units are weight percent dry basis after ignition

Table 1. Bulk chemical analysis for a typical filler-grade fly ash.

VISCOSITY

Consider a mixture of molten asphalt with a filler and the influences that affect the resulting viscosity at any given weight percent loading. First, there is an asphalt demand to wet out each individual particle's surface. Second, additional asphalt is required to fill the voids between adjacent particles. Only then will the addition of additional asphalt yield sufficient particle separation for the system to achieve flow and subsequently lower viscosity. This scenario is further complicated by the filler's particle shape and surface properties. Therefore, in any given asphalt, the driving influences on viscosity attributed to the filler are: shape; size distribution; surface characteristics, such as reactivity and porosity; and density.

■ *Shape*—Fly ash particles are spherical. Limestone's shape is "blocky" with highly irregular fractured surfaces. The sphere is the geometric shape that presents the minimum surface area for any given volume, thus minimizing the amount of asphalt necessary to wet out the surface. The spherical shape also allows for easier movement as the particles flow by each other in a dynamic system. Figures 1 and 2 show particles of typical filler-grade fly ash and limestone, respectively.

■ *Size distribution*—Through the selection and processing of certain sources of fly ash, one can obtain the trimodal particle size distribution illustrated in Figure 3. Note that the peaks in this distribution are centered on 1-, 10-, and 100-micron (0.04-, 0.4-, and 4 mils-) diameters. This distribution results in extremely efficient particle packing such that the amount of asphalt required to fill the voids between adjacent particles is at a minimum.[7] A typical limestone filler size distribution is shown in Figure 4.

■ *Surface characteristics*—The surface of a filler-grade fly ash particle is hard, glassy, nonporous, and relatively nonreactive. In contrast to limestone, fly ash will not absorb any of the oily components of asphalt. This difference in surface properties would influence not only the viscosity, but also presumably would affect the aged filled coating properties.

■ *Specific gravity*—The specific gravity of limestone typically runs in the 2.65 to 2.70 range while filler-grade fly ash typically has a specific gravity of 2.45 to 2.55.[6]
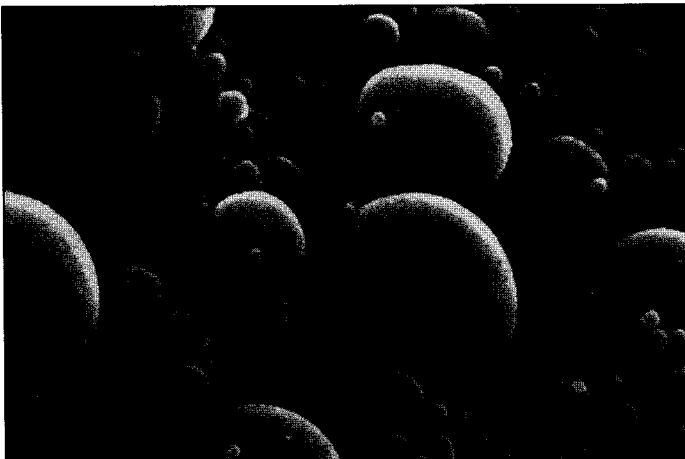

Figure 1. Micrograph of filler-grade fly ash showing typical spherical particle shape (magnification=1,000x).
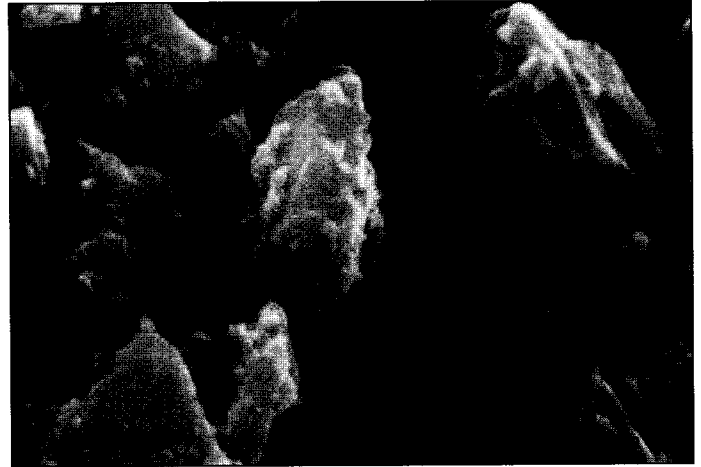

Figure 2. Micrograph of limestone filler showing blocky, irregular particle shape (magnification=1,000x).
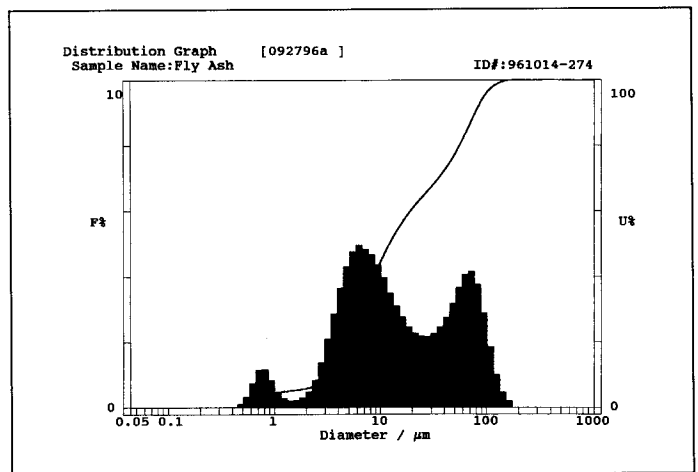

Figure 3. Typical particle size distribution of filler-grade fly ash showing trimodal distribution. The median diameter is 0.5 mil (12.05 microns) with a specific surface area of 997.4 mm²/mm³ (25,334 in²/in³). The left axis (F%) is the frequency percent (histogram); the right axis (U%) is the cumulative percent finer than (solid line).
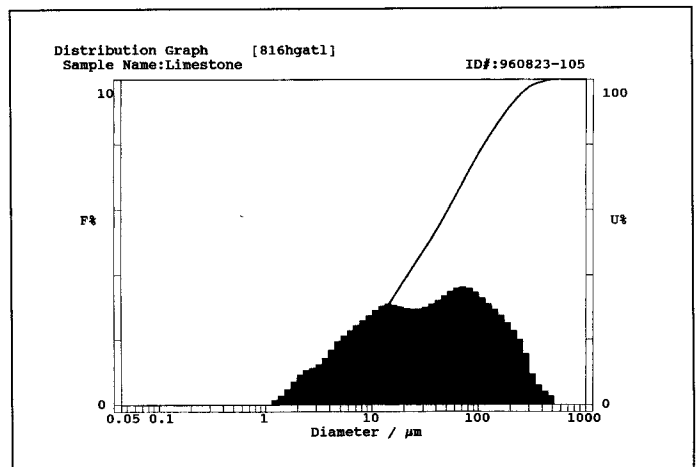

Figure 4. Typical limestone particle size distribution. The median diameter is 34.22 microns (1.5 mil) with a specific surface area of 461.3 mm²/mm³ (11,717 in²/in³). The left axis (F%) is the frequency percent (histogram); the right axis (U%) is the cumulative percent finer than (solid line).
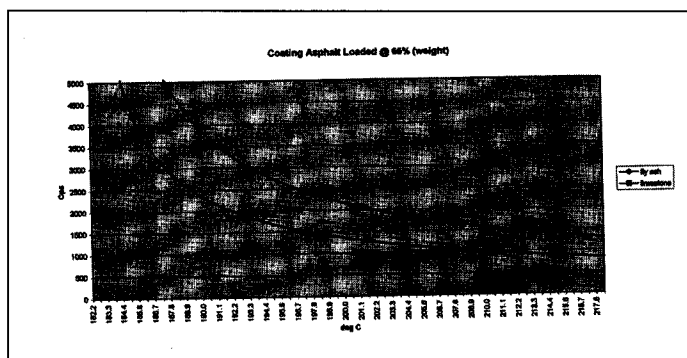
Figure 5. Viscosity curves for fly ash and limestone loaded at 65% (weight) in the same coating grade asphalt (Cps=Centipoise).
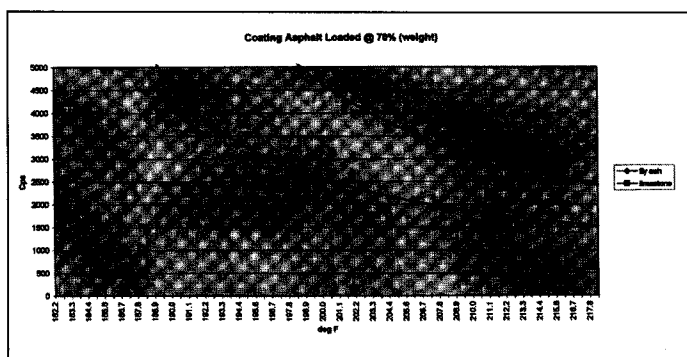

Figure 6. Viscosity curves for fly ash and limestone loaded at 70% (weight) in the same coating grade asphalt (Cps=Centipoise).

The net result of these factors is a compound viscosity difference illustrated in Figures 5 and 6 in which fly ash shows a >30 percent lower viscosity throughout a shingle manufacturing plant's typical formation temperature and filler loading ranges. The practical implications of this temperature/ viscosity advantage for fly ash is better sheet formation at higher production speeds.

SPECIFIC HEAT

Typical operating temperatures during the coating process in shingle manufacture are 200°C (392°F) or higher. The filler is heated prior to mixing with asphalt. A subsequent cooling process is needed before the shingles can be cut. Fly ash has a heat capacity (C_p) of 0.62 to 0.65 while limestone's values range from 0.83 to 0.91 (values expressed in J/°K-gm at 200°C [392°F]).[6] As a result, approximately 30 percent less energy is required to heat fly ash to the required processing temperature relative to limestone. The lower C_p also allows for more rapid cooling prior to the shingle cutter. This effect, coupled with the temperature/viscosity considerations discussed previously, has allowed for production speed increases of >10 percent in plants using fly ash compared to limestone.

SIMULATED WEATHERING/UV EXPOSURE

Shingles are sold to consumers with warranty periods ranging from 20 to 40 years. The manufacturer has a significant economic liability for the product during this time. A common laboratory evaluation used to give an indication of relative weathering performance between various unfilled asphalts
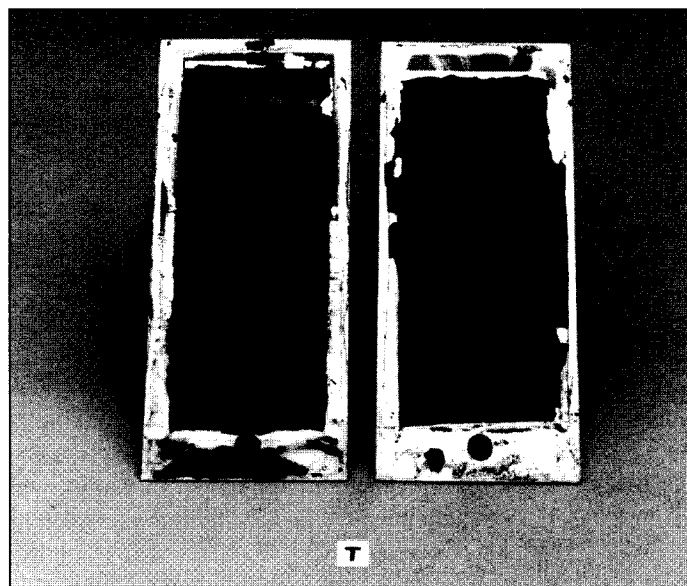

Figure 7. Simulated weathering/UV exposure panels after 2,000 hours of side-by-side exposure. The panel on the left contains 65% (weight) limestone filler; the panel on the right contains 65% (weight) fly ash filler.

and between different fillers in filled coating mixtures is simulated weathering/UV exposure, described in ASTM D 4798.

The traditional evaluation procedure of exposed simulated weathering/UV exposure panels is to detect cracks in the filled coating asphalt by using a sparking device as described in ASTM D 1670. This method is not feasible for fly-ash-filled coatings because of the metal content of the ash. However, careful visual examination, both with and without magnification, provides significant contrasts for comparison purposes.

Figure 7 is a photograph of two panels prepared with the same commonly used coating asphalt and exposed side-by-side in the same simulated weathering/UV exposure chamber for 2,000 hours. The panel on the left contains a limestone filler that has been used extensively in shingle manufacture while the right panel contains filler-grade fly ash. Both loadings are at 65 percent by weight. Although the fly ash panel shows some degree of surface cracking and crazing, the limestone panel exhibits numerous fissures completely through the filled coating film, exposing the underlying metal.

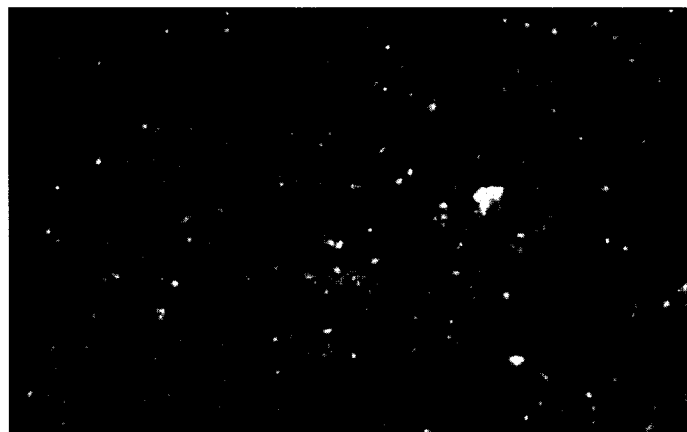Figures 8 and 9 shows similarly prepared panels (same

Figure 8. Simulated weathering/UV exposure panel under 40x magnification of 65% (weight) fly-ash-filled coating after 1,500 hours of exposure.
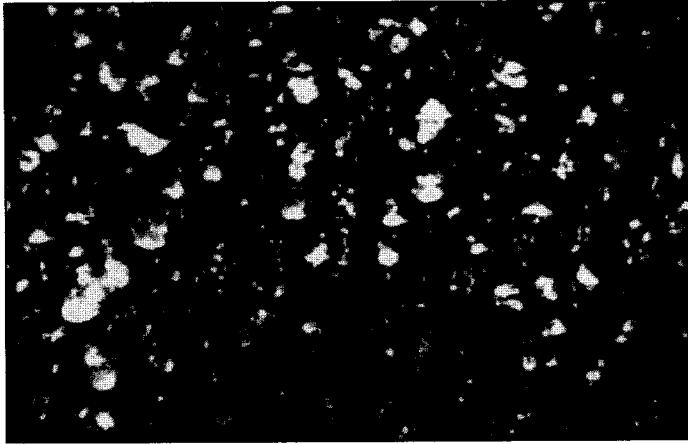
Figure 9. Simulated weathering/UV exposure panel under 40x magnification of 65% (weight) limestone-filled coating after 1,500 hours of exposure.

asphalt, weight loading, simulated weathering/UV exposure chamber, etc.) after 1,500 hours of exposure under 40 power magnification. One could postulate that the observed differences in these surfaces include fly ash's opacity to ultraviolet (UV) light, the tendency for limestone to absorb some of the oily components of asphalt, and the efficiently packed matrix inherent in the fly ash particle size distribution.

MECHANICAL PROPERTIES

The important mechanical properties of filled coating include tensile, elongation, pliability, tear resistance, and modulus of elasticity. Of interest to the shingle manufacturer is how these properties compare both before and after aging.

At the author's request, a study was conducted at Center for Applied Engineering in St. Petersburg, Florida, blending a limestone filler and fly ash filler loaded at 65 percent (weight) into the same asphalt. Coupons measuring 25 mm by 150 mm by 0.625 mm (1 inch by 5.9 inches by 0.02 inches) were cast to measure tensile and elongation. Beams 200 mm (7.9 inches) long with a 13-mm (0.51-inch) square cross section were cast to measure modulus. These films and beams were tested both before and after aging in a dark, humid oven at 70°C (158°F), 95 percent R.H. for 35 days. Tensile and elongation tests were conducted at 23°C (73°F) in a universal machine, jaw separation of 75 mm (3.0 inches),

	Fly Ash		Limestone	
	Not Aged	**Aged**	**Not Aged**	**Aged**
Tensile, kgf/mm²				
Mean	0.0472	0.1169	0.0479	0.1107
StdDev	0.0044	0.0151	0.0024	0.0150
# samples	20	10	20	10
% Elongation				
Mean	11.57	2.15	10.79	1.98
StdDev	2.25	0.34	1.08	0.35
# samples	20	10	20	10
Modulus, kgf/mm²				
Mean	1.415	3.809	0.977	3.772
StdDev	0.170	0.403	0.139	0.708
# samples	12	8	9	10

Table 2. Test results for asphalt-containing limestone filler and fly ash filler.

crosshead speed of 13 mm/minute (0.51 inches/minute). Modulus was measured at 23°C (73°F) in the universal machine equipped to measure flexural three-point bend strength on a 150-mm (5.9-inch) span with a crosshead speed of 25 mm/minute (1 inch/minute). The results are shown in Table 2.[6]

Examination of the results showed comparable tensile and slightly better elongation for the fly ash samples. The modulus results are interesting in that the unaged fly ash beam started out 45 percent higher than the limestone beam. This unaged difference in modulus is presumably due to the efficiently packed particle matrix inherent in the fly ash. After aging, the modulus increase in the fly ash beam was 269 percent versus an increase of 386 percent for the limestone beam. One could postulate that the stiffening, or hardening, differences seen after aging are related to the particle surface characteristics and reactivities.

TEAR RESISTANCE

Establishing a solid relationship between the use of fly ash vs. limestone and the subsequent effect on tear resistance (as per ASTM D 3462) has been difficult. The author's personal experience with attempting to adequately simulate a tear test using laboratory-prepared samples, which give a good correlation to tests conducted on actual shingle production, have not been successful. Further, references that report success with this particular lab sample/production sample correlation are not known. Consequently, one is left with the evaluation of actual production samples in order to define the relationship between tear resistance and how it is impacted by different fillers. As one tests production samples from any given roofing plant, variations inherent in the fiberglass mat, and difficulties in obtaining identical filler loadings, finished product weights, and the balance between top coating and back coating can add to the complexity of isolating the effects of one filler against another. Tables 3 and 4 provide

	Fly Ash	Limestone
% Filler (wt.)	63.9	63.5
CMD Tear, g	1550	1514
Std. Dev.	201	187
# samples	9	10
% Filler (wt.)	65.7	66.5
CMD Tear, g	1277	1475
Std. Dev.	254	135
# samples	10	10
% Filler (wt.)	71.2	68.8
CMD Tear, g	1120	1386
Std. Dev.	161	275
# samples	10	10

Table 3. Results of tear resistance testing using production samples from a roofing plant.

	Fly Ash	Limestone
% Filler (wt.)	68.9	67.3
CMD Tear, g	1230	1642
Std. Dev.	185	272
# samples	40	40

Table 4. Results of tear resistance testing using production samples from a second roofing plant.

the test results for production samples from two roofing plants.

It would appear that there may be a negative effect on tear attributable to switching from limestone filler to fly ash within certain specific raw material compositions. In an attempt to better understand the significance of these results, an examination of the reproducibility and repeatability of the test was made.

The test method for tear resistance in ASTM D 3462 was derived from ASTM D 1922, "Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method." The plastic film test was modified in such a way that the tear resistance of fiberglass shingles could be measured.

Paragraph 1.2 of D 1922 reads: "Because of (1) difficulties in selecting uniformly identical specimens, (2) the varying degree of orientation in some plastic films, and (3) the difficulty found in testing highly extensible or highly oriented materials, or both, the reproducibility of the test results may be variable and, in some cases, not good or misleading."

Paragraph 13.2 of D 1922 states: "Bias cannot be determined as there is no absolute standard that can be used as a reference."

It is important to realize that ASTM D 1922 is meant to test monolithic plastic films, and yet the above statements are a necessary part of the standard. When considering a fiberglass shingle, one has a composite material containing at least five separate components along with a directional orientation.

Numerous tear resistance tests and round robin studies have been conducted within the Asphalt Roofing Manufacturers Association (ARMA) Research Committee over the past decade. One of these was a round robin test performed in 1993 on three different samples and tested by eight different laboratories, all using a 7.1-lb. (3,200-gm) pendulum. The data was analyzed in accordance with ASTM E 691. Results are listed in Table 5.[2]

So the question remains: Is there a measurable effect on tear between limestone filler and fly ash filler? Statistically, the answer is no. The inherent limitations of this test called out in ASTM D 1922 and reinforced by the ARMA round robin data make drawing any conclusions a questionable practice. Intuitively, one would think that there must be some effect. Certainly the morphology of limestone vs. fly ash plays a part as the blocky, irregular crushed rock particle would offer more shear resistance than the spherical fly ash particles. Also, one would expect the difference in absorption between the two types of particles to have an effect. It seems possible that when considering the asphalt/filler interaction, there may be an inverse relationship between tear resistance and long-term pliability. As has been stated by other authors, pliability as a function of age is the most important factor in long-term shingle performance.[8] It is the author's hope to conduct future research to more ably describe the asphalt/filler particle surface interactions that may shed additional light on this relationship.

Sample	Average CMD Tear, G	95% Repeatability	95% Reproducibility
A	1515	616 (41%)	718 (47%)
B	1766	783 (44%)	792 (45%)
C	1576	836 (53%)	866 (55%)

Table 5. Results of a 1993 ARMA round robin test.

ALGAE RESISTANCE

Many people are aware of the dark, streaky discoloration found on shingle roofs, particularly in warm, humid climates. This discoloration is caused by the growth of several different species of algae and bacteria. Observations of roofs with this problem will show that those areas of the roof beneath zinc or copper flashings are void of the growth. Subsequent research has shown that there are several metal ions that will inhibit the growth of these organisms. Some years ago, it was postulated that calcium carbonate acted as a catalyst for the growth of the microorganisms that cause this discoloration. It is not uncommon for limestone-filled shingles applied in the southern coastal states to exhibit this discoloration as quickly as two years after application.[4]

Particular attention is being paid to two roofs composed of fly-ash-filled shingles in Baton Rouge, Louisiana, and Tampa, Florida. After four years of exposure, there is no evidence of discoloration on these roofs while many neighboring houses with similarly aged roofs are showing significant discoloration.

FUTURE WORK

Many years of manufacture of asphalt shingles using predominantly limestone fillers has influenced the perception of what the idealized coating asphalt specification should be with respect to functional chemical analysis, ductility, viscosity, softening point, and penetration, in addition to what viable filler loading levels are. Also, as discussed in the tear resistance section, a greater understanding of the asphalt/filler interaction and its effect on long-term pliability is an important consideration. It is obvious that fly ash is a fundamentally different filler than limestone. It is possible that coating asphalt specifications may be able to be modified to take full advantage of these unique properties in such a way to offer improved performance at greater economies.

REFERENCES

1. Asphalt Roofing Manufacturers Association industry shipment data, 1995.
2. Asphalt Roofing Manufacturers Association Research Committee, unpublished work.
3. Petersen, J. Claine. *Chemical Composition Of Asphalt As Related To Asphalt Durability—State Of The Art*, presented at the 63rd Annual Meeting of the Transportation Research Board, January 1984.
4. George, Bennerman, and Cochran. 3M Study, 1987.
5. Hemmings, R. T. and E. E. Berry. "On The Glass In Coal Fly Ashes: Recent Advances," *Materials Research Society Symposium Proceedings*, Volume 113, 1988.
6. Shaw, D. E. Unpublished work.
7. Allen, T. *Particle Size Measurement*, 3rd Edition, Chapman and Hall Ltd., London, UK, 1981.
8. Noone, M. J. and W. K. Blanchard. "Asphalt Shingles—A Century Of Success And Improvement," *Proceedings of the 10th Conference on Roofing Technology*, 1993, 23-33.