DIE DROOL
IN CHEMICALLY CROSSLINKABLE POLYOLEFIN COMPOUNDS

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ABSTRACT

Die drool is a commonplace, sometimes chronic, processing problem that can have serious effects on the final quality and appearance of extruded products, including wire and cable constructions. A laboratory scale test for assessing the severity of die drool for a given compound has been developed. In this study, the effects of several extrusion parameters on the die drool generation of an automotive wire insulation compound were examined. It was found that die condition, particularly the presence of damage and defects in the die surface, strongly influenced the rate of die drool. In addition, the rate of die drool was found to increase at higher extrusion rates and temperatures. Die cooling was found to be effective in reducing the rate at which compounds generated die drool.

INTRODUCTION

The undesirable accumulation of material around the exit of an extrusion die is commonly referred to as die buildup or die drool, and it is observed in a wide variety of polymer systems and extrusion processes. Die buildup can be particularly problematic in processes employing the continuous vulcanization (CV) technique, such as the insulation of automotive primary wiring. This buildup occurs because the die is enclosed by a tube filled with high pressure steam and, thus, is inaccessible during the wirecoating operation, preventing removal of the accumulating material by the operator of the line.

Eventually, die buildup releases from the die face in one of two ways. The buildup can attach to the wire insulation in the form of a complete or partial ring of material (as shown in Figure 1), commonly referred to in the wire and cable industry as a die ring, horsecollar, donut, or fuzzball. In addition to causing tears or other flaws in the wire insulation, these rings can create problems in the automated harnessing operation, causing wire breaks and downtime. Die buildup which does not adhere to the insulation eventually falls into the CV tube and is washed down the tube by steam condensate. If the die drool is only partially crosslinked when it detaches from the die face, numerous particles can adhere to one another, forming large pieces which can clog steam traps, screens and water seals and result in unscheduled shutdowns.

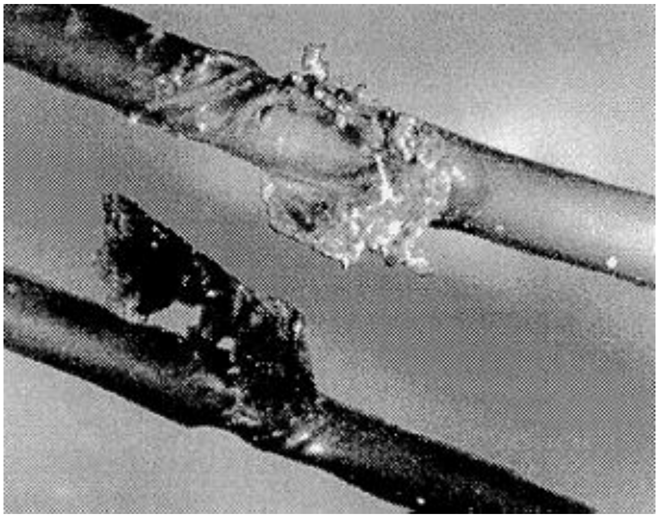

Figure 1: Two automotive wires having processing defects resulting from die buildup

In general, die buildup is a widely experienced, seldom studied phenomenon. While a wide variety of causes and aggravating factors for die buildup have been proposed, the basic mechanism is still not understood. A number of factors which have been proposed as sources of die buildup are [1]:

1. Low molecular weight polymer species
2. Volatiles, including moisture
3. Presence of a filler material
4. Poor dispersion of pigments
5. Draw down and take off rates
6. Amount and rate of die swell
7. Atmospheric conditions including humidity
8. Die exit angles, land length, and land entrance size
9. Dissimilar component viscosities
10. Die condition (including cleanliness, presence of damage, defects, etc.)
11. Pressure fluctuations in screw channel
12. Improper melt temperature

Although many of these factors appear to aggravate die buildup, it appears that none of them is the actual root cause.

While it is true that unfilled polymers will produce die buildup under certain circumstances, highly filled compounds generally produce die buildup at a substantially higher rate and at much lower temperatures than the unfilled base resins. The level of filler in the compound appears to have a strong influence on the rate at which the compound generates die drool, probably due to interactions between the filler and the polymer. Whether these filler-polymer interactions are physical or chemical in nature is unknown. The high filler levels present in automotive primary wire insulation compounds make these compounds highly prone to die buildup problems.

The base resin of the compound being extruded also influences the rate at which the compound generates die buildup. Even similar polymers produced on different reactor types sometimes generate die buildup at different rates. This difference in die buildup rate may be due to different levels of low molecular weight species in polymers produced on different reactors.

One of the few attempts in the literature to address the causes of die buildup is a brief article by Klein[2], in which die buildup is attributed to extrudate swell. Klein hypothesized that die buildup occurs when the extrudate swells so severely that molten polymer scrapes against and adheres to the surface of the die. The logical extension of this reasoning is that die buildup can be minimized by minimizing the tendency of the resin or compound to exhibit extrudate swell.

There are some contradictions to the theory that die swell and die buildup are directly related, however. The incorporation of a rigid filler into a polymer melt reduces the normal stresses during extrusion[3,4]. The result of the reduction of normal stresses is that polymers exhibit less extrudate swell when filled, whereas filled polymers typically exhibit more severe die buildup than the corresponding base polymers.

Some techniques for alleviating die buildup are known in the patent literature. For example, the addition of fluoropolymer processing aids to a resin or compound can sometimes reduce or even entirely eliminate die buildup[5]. Unfortunately, the function of the fluoropolymers can be inhibited by some other additives, especially in highly filled compounds[6,7]. There appear to be no general principles known for designing compounds that are resistant to the formation of die buildup.

Coating the die surface and in the interior of the die with lubricious materials such as fluoropolymers or polysiloxanes has also been found to reduce die buildup for some systems, although the useful life of such coatings can be quite short when highly filled compounds are extruded [8,9]. Manufacturers have devised dies utilizing mechanical means (such as pins) of breaking up the material accumulating at the die exit[10]. It is also known that cooling of the die helps reduce or even eliminate die buildup in wirecoating operations[11].

A serious obstacle to a deeper understanding of the variables controlling die buildup is the lack of a reliable laboratory scale test method which can predict the tendency of a compound to exhibit die buildup. Experiments performed on commercial scale equipment are typically narrow in scope, due to expense. Die buildup is often an intermittent phenomenon, varying not only day to day, but also from lot to lot of compound, and from extruder to extruder (or even between various constructions on the same extruder). Most published studies of die buildup are qualitative rather than quantitative in nature.

Two quantitative techniques for assessing the rate of die buildup are found in the literature. Kurtz, et. al. scribed circles on the face of the die, designating 25 percent increments of die face cross sectional area[6]. The times required to cover various fractions of the die surface were used as a measure of die buildup rate. Since die buildup does not always advance across the die face in a uniform front, the time to cover a designated area can be somewhat variable, and this technique was not considered in this study.

In the second method of die buildup measurement described in the literature, Chan collected and weighed the amount of die buildup which attached to the extrudate as a function of time[12]. This method was not an actual measure of die buildup rate, however, as the amount of material remaining on the die surface was not quantified. This technique was adapted for the current study, but it was found to have deficiencies and was discarded.

This paper presents a description of a laboratory scale test to assess the level of die buildup as a function of compound and process variables.

EXPERIMENTAL PROCEDURES

- ### MELT INDEX DIE SWELL (MIDS) TEST

  Extrudate swell was measured using an extrusion plastometer (ASTM D1238) fitted with a short-landed die. The plastometer temperature was 125°C. The die used had a diameter of 0.0824 inches and a length of 0.028 inches. Samples weighing five grams were preheated under a 2,000 g load for 6 minutes before initiation of the test. Testing load was 5000, 10,000 or 20,000 grams. Six inches of extrudate were obtained and discarded, then another six-inch length of extrudate was collected, cooled for one hour and measured at the center and one inch from each end. Three specimens for each compound were tested in this way and all measurements averaged to obtain extrudate diameter. The swell ratio is the ratio of extrudate diameter to the die diameter.

- ### ACCUMULATION RATE MEASUREMENTS

  Compound was extruded through a ¾-inch laboratory extruder (hereafter referred to as Extruder 1) equipped with a screw having an L/D of 20/1 and a compression ratio of 1:1. The die used had a diameter of 0.075 inches and was a crosshead wirecoating die in which the guider tip was blind (i.e., the end of the guider tip was blocked to prevent backflow of material into the guider).

  The measurements were performed by extruding compound at 100 RPM for 10 minutes, then shutting off the extruder and carefully collecting the accumulated material from the face of the die. The extrudate and die buildup were weighed and a ratio of the weights calculated. The extruder was purged for 10 minutes between shutdown for sample collection and the initiation of a new test. Thirty-minute purges were conducted when changing compounds.

DIE BUILDUP TEST DEVELOPMENT

- ### ELEVATED DIE FACE TEMPERATURE EXPERIMENTS

  The technique employed by Chan required some modification to implement, as die buildup does not attach to the extrudate during thermoplastic extrusion of commercial automotive wire insulation compounds. For this reason a shield was placed around the strand die mounted on Extruder 1 and a heat gun was directed past the die to raise the air at the die face to a temperature of 350-400°F. In this configuration die buildup occurred at a much faster rate than during thermoplastic extrusion, and the material accumulating at the die exit periodically broke free and attached to the extrudate in a process illustrated in Figure 2.

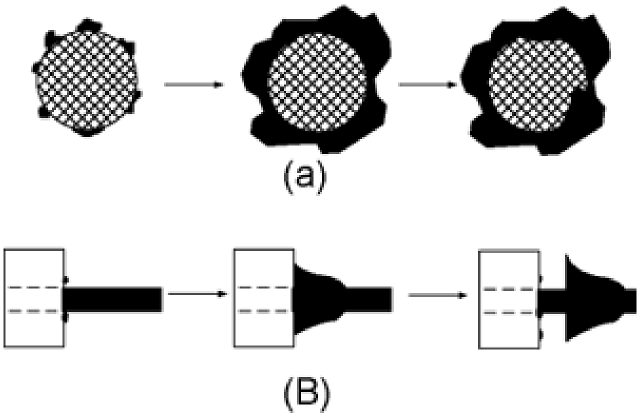

Figure 2. **Illustration of the die ring formation process, shown from two perspectives: (a) front view of die exit, (b) side view of die face. Material accumulates at die exit, forming a coherent ring, which eventually crosslinks and attaches to the extrudate.**

Unfortunately, the time required for detachment of the die buildup was excessive (one hour or more for each event) and very irreproducible. Therefore, this technique was also abandoned. However, several qualitative observations were made in the course of these experiments. In thermoplastic extrusion, the material accumulating at the die exit is continuously pushed aside by fresh material, causing the buildup to spread out in a thin layer across the entire die face. When the die face temperature is sufficient to quickly crosslink the die buildup, the fresh drool builds a conical deposit projecting off the die face along the length of the extrudate. Eventually, the deposit begins to occlude the opening of the die, placing enough stress on the die ring to force it off the face of the die.

■ EXTRUDATE SWELL MEASUREMENTS

In order to investigate Klein's theory of the relationship between die buildup and extrudate swell, the MIDS test was performed on three commercial automotive wire insulation compounds: A, B and C. From evaluations on industrial scale equipment, the compounds were known to have different tendencies to exhibit die buildup: Compound A showed a moderate level of die buildup, Compound B showed a slight level of die buildup and Compound C showed virtually no die buildup.

The swell ratio as a function of melt flow rate for each of the three commercial compounds is shown in Figure 3.

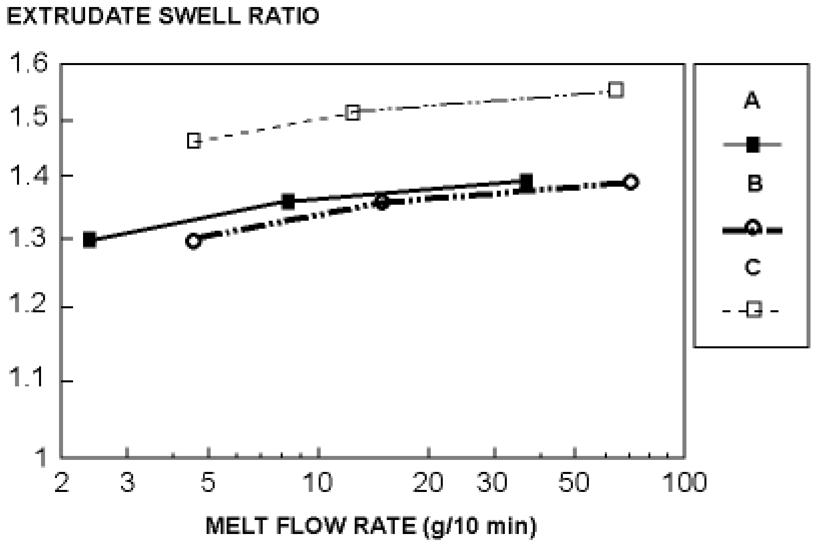

Figure 3. **Extrudate swell ratio as a function of melt flow rate for three commercial automotive wire insulation compounds. The melt flow rate was varied by imposing three different loads (5000, 10000 and 20000 grams).**

Compound C, which in practice exhibits the lowest level of die buildup, shows the most severe extrudate swell behavior. There is little difference in the extrudate swell behavior of Compounds A and B, even though their tendencies to exhibit die buildup are quite different. These results indicate that extrudate swell is not correlated to the die buildup behavior of these compounds.

■ ACCUMULATION RATE MEASUREMENTS

Die buildup rate was assessed through direct collection and weighing of the material accumulating on the die face. Since the amount of die buildup would clearly increase with the amount of compound extruded, the die buildup rate was expressed as the ratio of the weight of accumulated material to the weight of compound extruded.

The accumulation rate method has some distinct advantages over the measurement of the time to cover the surface of the die. The direct measurement of the quantity of material deposited on the die face is more objective than the judgment of coverage time and also accounts for the three-dimensional nature of the deposit. However, the weights obtained are very small (typically in the range of 5-25 mg for a 10 minute run), so the detachment of the die ring must be painstakingly performed and a reliable analytical balance is essential.

A series of three such measurements using Compound A is shown in Figure 4. Following the standard procedure, die buildup rate was measured for a 10-minute period with the extruder being purged for 10 minutes between runs. A series of measurements was also carried out in which the extruder was shut down and allowed to sit idle for 10 minutes between runs without purging. There was a slight increase in the rate of die buildup when the compound was allowed to sit in the extruder, indicating that residence time has an effect on the rate of die buildup. This effect may be due to thermal degradation of the polymer or some other component of the compound at the processing temperature.

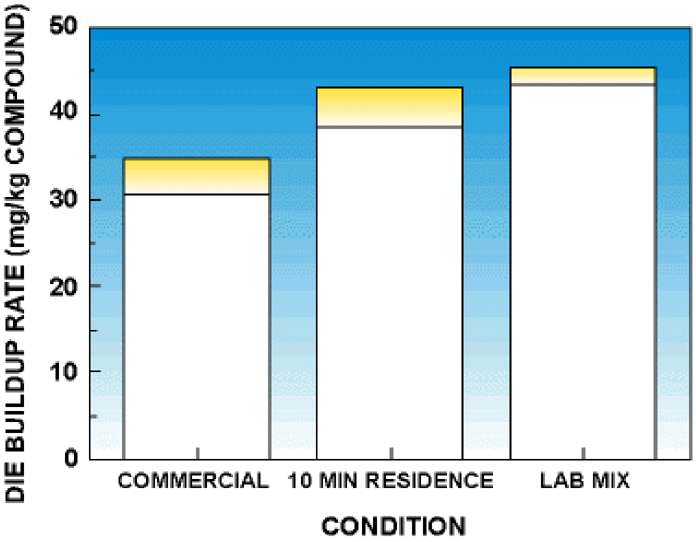

Figure 4. **Mass accumulation rate as a measure of die buildup rate, showing the effects of residence time in the extruder and laboratory versus commercial scale mixing equipment. The stack bars indicate the 95% confidence limit.**

In the third set of measurements, it was seen that material compounded on a small laboratory mixer showed a higher rate of die buildup than material produced on a commercial scale mixer. This comparison indicates that mixing has an effect on the die buildup behavior of the compound. Whether this effect is due to differences in the quality of mixing or due simply to differences in shear or thermal history between the lab and commercial equipment is not known.

Figure 5 shows the die buildup rate as a function of output rate for two different 3/4-inch laboratory scale extruders (designated Extruder 1 and 2). The temperature profile for both extruders was set to a flat 250°F. For both extruders, the die buildup rate increased with increasing output rate, even though the die buildup rate is normalized on the mass of extrudate. This increase could translate into a larger number of defects on a given quantity of wire as production rates are increased.

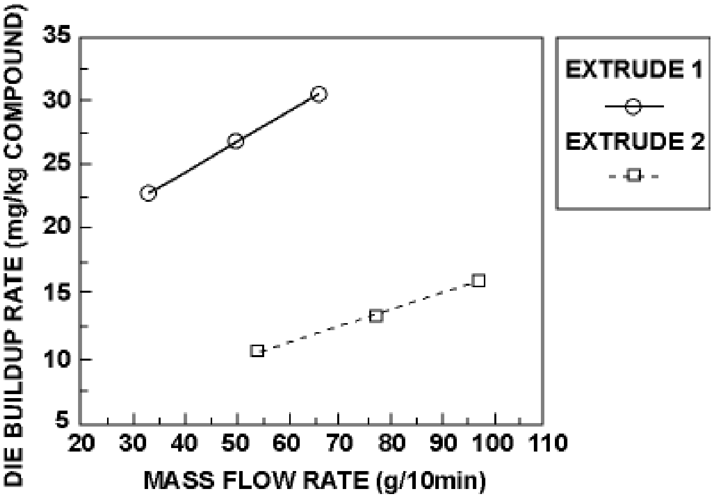

Figure 5. Die buildup rate of compound A as a function of extruder output for two different 3/4-inch laboratory extruders. The same die and head were used on each extruder.

The die buildup rate was significantly higher on Extruder 1 than Extruder 2 at comparable output rates. The same die and head were used on each extruder for these experiments, but the two extruders are quite different in several respects. Extruder 1 has an oil heated barrel with a single control zone and no cooling, while Extruder 2 has an electrically heated, 3-zone barrel with air cooling. The thermal history of the compound within each extruder is thus different, and this difference could account for the difference in die buildup rate. The screw of Extruder 1 has an L/D of 20/1 and a compression ratio of 1:1, while the screw of Extruder 2 has an L/D of 26/1 and a compression ratio of 4:1.

It is likely that the higher die buildup rate on Extruder 1 is due to the lack of barrel cooling on that extruder. This situation is observed frequently in industrial practice, where die buildup tends to occur to varying degrees on different lines, even when running the same compounds and constructions. It also indicates that general application of this method of assessing die buildup requires that control compounds be used when comparing data obtained on different extruders.

Since neither of the extruders were equipped with die cooling, that variable could not be examined in depth. However, a simple arrangement was constructed in which plastic tubing connected to an in-house air supply was set to blow across the face of the die for cooling. This experiment was carried out on both extruders running at a screw speed of 100 RPM. Instead of generating die rings of approximately 20 mg in 10 minutes, Extruder 1 generated so little die buildup after 1 hour that the buildup could not be accurately detached for weighing. A similar reduction was observed for Extruder 2. This experiment illustrates the dramatic reduction in die buildup that can be obtained with die cooling.

In order to ascertain the relationship between die buildup generated on a small laboratory extruder and to the rate of die buildup on a commercial line, three compounds with differing levels of die buildup generation were formulated. Die buildup rate measurements were made in the laboratory, and similar measurements were carried out on a 3½-inch commercial wire line with the CV pulled away and the wire removed to provide the same test geometry as the laboratory extruder. Figure 6 shows the laboratory-measured die buildup rate as a function of the die buildup rate measured on the commercial line.

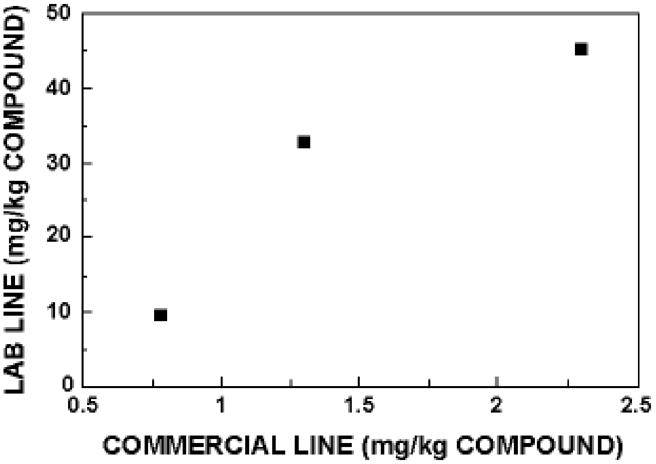

Figure 6. A comparison of the rates of die buildup measured on a 3 1/2 -inch commercial wirecoating line to those measured on a 3/4-inch laboratory extruder.

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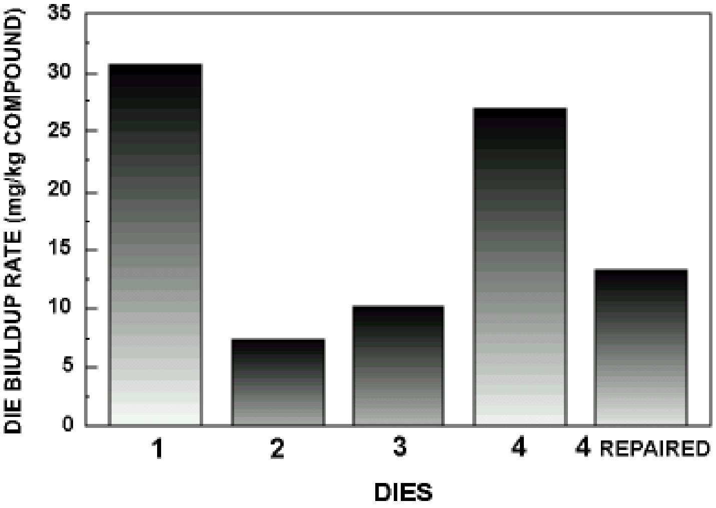

Figure 7. **Comparison of die buildup rate measured on four dies of identical design. The dies were: (1) a heavily used die, (2) a previously unused die from the same manufacturer, (3) an unused die from a different manufacturer, (4) a defective die with a burred exit.**

Dies 3 and 4 were produced by a different fabricator from the same materials as the first two dies. Die 3 was properly fabricated, but the hole in Die 4 was not drilled completely through the die, leaving a ridge of burred material approximately 0.05 inches wide which partially occluded the die exit. The die buildup rate for the defective die was substantially higher than that of the normal die. Die 4 was then repaired by completing the course of the die opening, which resulted in a die buildup rate similar to that obtained with Die 3.

The final variable examined in this study is the effect of die construction material and surface treatment on die buildup. As mentioned previously, certain types of die surface treatments (e.g., teflon coating) have been shown to decrease die buildup. However, such treatments are expensive and short-lived, making them commercially unattractive. There are other surface treatment techniques which decrease surface roughness, improve the corrosion resistance of the metal and actually increase the service life of the die. The effects of these treatments on die buildup have never been reported in the open literature.

For this experiment, a set of identical dies was fabricated from untreated 600 and 420 stainless steel. The 420 SS dies were subjected to nitride, chrome plating and cryogenic surface treatments. The nitride and chrome plating treatments provide smooth, hard surfaces, while the cryogenic treatment provides a very hard but slightly rough surface. The 420 stainless steel was selected because it is one typically used in the construction of automotive wirecoating dies. The 600 stainless steel was selected because it is a harder, more corrosion-resistant material than the 400 series steels.

All of the fabricated dies were placed in an ashing furnace for 2 hours at 700°F and 25 in Hg vacuum and then cleaned in an ultrasonic bath before use. This cleaning was to remove any residual oils and debris remaining on the die surfaces from the fabrication process. It was observed that such residues can increase the die buildup rate initially observed when extruding with a given die, resulting in a time dependent die buildup rate. This phenomenon is shown in Figure 8 for one of the untreated 420 SS dies, where the die buildup rate varied over time, eventually reaching a plateau when the residue on the die had been purged away.

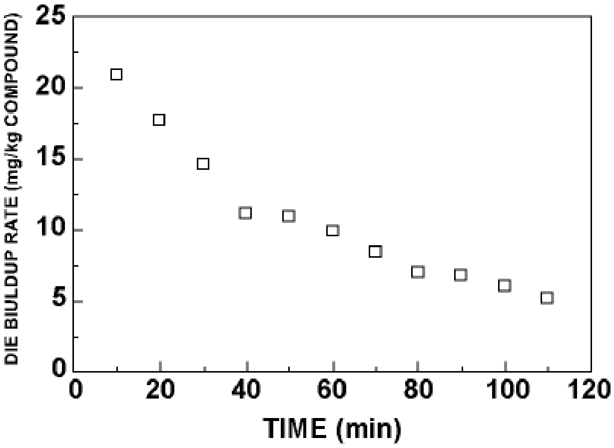

Figure 8. **Die buildup rate as a function of time for an untreated 420 stainless steel die as received from the manufacturer. The time dependency of the die buildup rate is an artifact of residues from the die fabrication process.**

The die buildup rates for the various dies after cleaning are shown in Figure 9. There are some apparent differences between the various surface treatments, but the two untreated dies showed the lowest rate of die buildup. This experiment seems to indicate that die buildup cannot be eliminated through the use of standard metal surface treatments, although more sophisticated coating techniques are known to be effective in reducing die buildup.

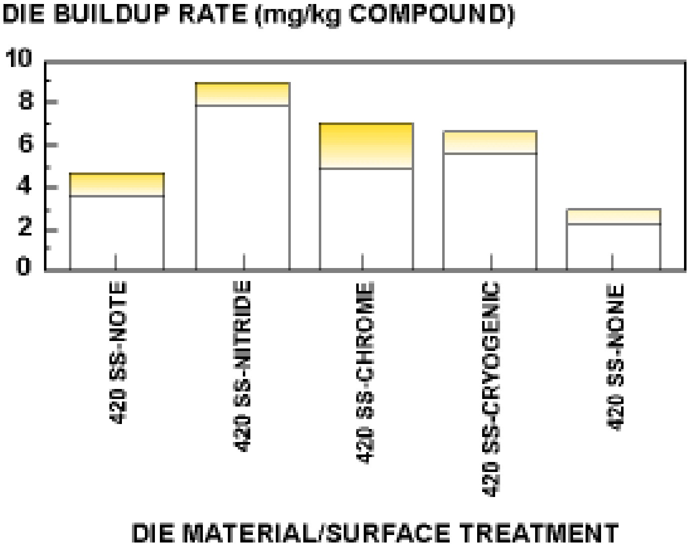

Figure 9. **Die buildup rate for Compound A extruded through dies having various surface treatments. The stack bars indicate the 95% confidence limit**.

CONCLUSIONS

A laboratory scale test for assessing the relative tendency of a compound to produce die buildup in commercial scale wirecoating operations has been developed. Applying this test, the following conclusions have been reached:

1. The rate of die buildup is increased by the presence of defects, scratches and gouges at the die exit.
2. Various extruders can exhibit very different die buildup rates, even when identical extrusion heads and dies are used.
3. Die construction materials and surface treatment appear to have an effect on the die buildup rate of extruded compounds. However, the lowest rate of die buildup seemed to be obtained with dies having no surface treatment.
4. Die cooling can dramatically reduce the rate of die buildup during extrusion.

REFERENCES

1. Gander, J.D. and Giacomin, A.J., "Review of Die Lip Build-Up in Plastics Extrusion," ANTEC 96, Toronto (May, 1996), pp.1113-1117.
2. Klein, I., "Die Drool: What Causes It, How to Avoid It", Plastics World, May, 1981.
3. Dealy, J.M. and Wissbrun, K.F., Melt Rheology and Its Role in Plastics Processing, Van Nostrand Reinhold, New York, (1989).
4. White, J.L., Czarnikci, L., and Tanaka, H., Rubber Chemistry and Technology, 53:823, (1980).
5. Priester, D.E. and Chapman, G.R., "Reducing Die Build-Up in Extrusion Applications," Polyolefins IX, SPE RETEC, Houston (February, 1995).
6. U.S. Patent 5,008,056 (1991).
7. Priester, D.E. and Stewart, C.W., "New Processing Additives for Polyolefins Minimize Formulation Interactions," SPE ANTEC, Detroit (May, 1992), pp. 2024-2028.
8. U.S. Patent 3,942,937 (1976).
9. U.S. Patent 2,403,476 (1946).
10. U.S. Patent 5,162,120 (1992).
11. Wooddell, G.L. and Itzkoff, M.L., "Crosslinkable Polyethylene for Wire and Cable: An Update," Wire Journal International (May, 1982), p. 62.
12. Chan, C.-M., "Viscosity and the Formation of Die Drool at the Polymer-Metal Interface: Effects of Surface Coatings," International Polymer Processing, X:3, pp200-203, (1995).

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