# Catalyst Particle Wetting and Breakup in Hydrazine Systems

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**An important relationship between catalyst reactivity in hydrazine and catalyst wetting and subsequent breakup has been established. In previous studies, wetting by liquid hydrazine had been shown to lead to gas pressure buildup in catalyst particles, followed under some conditions by particle fracture. In an experimental study, individual Shell 405 catalyst particles of various size and history were mounted in a flow reactor in which the effects of hydrazine temperature, flow velocity, and exposure time on wetting and breakup could be determined. Particle wetting has been found to be most strongly controlled by liquid hydrazine temperature; greatest wetting and breakup occur in particles exposed to lowest hydrazine temperatures. Wetting and breakup, however, are dependent upon size and history. Both wetting and breakup increase with decreasing as-received particle size. For catalysts heated in an inert atmosphere, apparently independent changes in wetting and breakup have been induced by various heating conditions, reflecting the complex relationship of the catalytic surface, pore characteristics and substrate strength.**

## Introduction

THE use of hydrazine catalytic reactors for a wide variety of extended life missions is presently limited by degradation of the catalyst particles as evidenced by breakup of the particles. Fracturing of a catalyst particle can be caused by large pressure gradients or thermal stresses which cannot be supported by the porous structure. Breakup caused by large pressure gradients has been illustrated under conditions in which liquid hydrazine wetting the outside surface of catalyst particles blocked the escape of gaseous decomposition products.[1] Wetting by the very reactive hydrazine results in gaseous decomposition product buildup near the gas-liquid interface. While the pressure buildup is very rapid, dissipation of pressure throughout the particle is slow because of the very small pore sizes and correspondingly high pressure drops. Pressure can be alleviated if: a) gas pushes liquid out of the pores; b) gas escapes from pores which have not been wet; or c) the particle fractures. The greater the tendency of the particle to wet and the higher the fraction of the particle which is wet, the more likely the particle is to fracture. In the current work, particle wetting has been shown to be related directly to catalyst reactivity in hydrazine. For a given catalyst particle, reactivity increases markedly with temperature, since the liquid hydrazine vapor pressure is very sensitive to temperature and it is the vapor which decomposes on the catalyst surfaces. For a set of particles, wetting is associated with the intrinsic activity of each of the particles – the lower the activity, the greater the likelihood of wetting.

In this experimental study, individual catalyst particles were mounted in a flow reactor in which the reactor temperature, hydrazine flow velocity and exposure time could be controlled. As-received, engine-fired, and heated particles have been tested to determine the general relationship between wetting and breakup and the effect of particle size and history on these phenomena.

## Experimental

In order to establish the relationship between wetting and breakup and the dependence of these phenomena on catalyst size and history, it is preferable to observe the behavior of individual particles. Shell 405 catalyst particles were exposed to hydrazine in the flow reactor shown schematically in Fig. 1. The body, internal parts, plumbing lines, and valves were stainless steel. A Teflon particle support and EPR O rings were used: the viewing window was Pyrex. Hydrazine was stored in a two liter stainless steel cylinder, pressurized with nitrogen, and metered through Matheson Series 600 flow meters. The hydrazine inlet line was maintained at reactor temperature.

The Teflon particle support rested in the holding fixture; particles were mounted with contact cement. A sliding sheath was dropped over the particle support to isolate the particles from the remainder of the reactor; the particle volume was evacuated with a mechanical pump while reactor temperature was stabilized. Hot and cold tap water were generally used to determine reactor temperature; for runs initially below cold water supply temperature, a circulating cooling bath was installed with 3-way valves to permit switching after test initiation. The reactor body temperature and liquid hydrazine temperature were measured with stainless steel-sheathed chromel-alumel thermocouples read directly on Omega readout meters. The entire conduct of a test could be observed through the viewing window. Motion pictures were taken using a Locam 16-mm camera with type 7241 Ektachrome film at framing rates of 50 to 500 frames per second.

When reactor temperature was stable, the particle volume was opened to atmospheric pressure, partially filled with mercury, and capped. Hydrazine flow was initiated and held a short time for purging. The camera, run at 500 frames per second, was manually started as the sheath was lifted. Particles were first exposed to hydrazine when mercury surrounding the particle flowed downward through the holding fixture into the spacer volume. Shortly after exposure of particles to liquid, the camera was stopped and reset for 50 frames per second.

Reactor temperature was slowly raised with short film segments taken at temperature intervals of 5° to 10°. When it appeared that any particle was nearing transition from the wetted to unwetted state, film was continuously run. The transition temperature and breakage (if any) of each particle were recorded.

This general procedure was used for all liquid immersion tests. Initial temperatures were usually 10° to 20° below the transition temperature and were as low as 31°F; maximum temperature of the water-heated reactor was approximately 110°F.

Particles of three sizes and a variety of histories were tested. The Air Force Rocket Propulsion Laboratory supplied samples of 14-18 mesh and 20-30 mesh from a test engine.[2] As-received particles of 8-12, 14-18, and 20-30 mesh size were used. Samples were heated in inert atmospheres to determine the effect of heating on wetting and breakup.

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Samples of as-received catalyst were heated under argon atmosphere in an electric furnace having a ceramic tube liner. For heating times of 2 hr or longer at 500° to 1000°F, samples were loaded into a cold furnace and left in place during heatup, soak and cooldown. For shorter heating times and lower temperatures, samples were loaded directly into the heated furnace, then moved after the appropriate time to a cool section of the ceramic tube and, after further cooling, removed from the liner.

## Results and Discussion

In the course of testing catalyst particles, observations were made of the following: rate at which gas was evolved by each particle; changes in the character of evolution; the temperature dependence of such changes; and breakage of particles. The most important factors determining wetting and breakup were found to be the hydrazine temperature, particle size and particle history.

In view of the temperature dependence of hydrazine vapor pressure, it would be expected that lowest gas evolution for any given batch of catalyst would be observed at lowest temperatures. This was found to be true for each sample; an illustration is given in Fig. 2. The rate of gaseous evolution upon initial exposure was qualitatively classified as slow, moderate or vigorous. Slow evolution was characterized by low-energy ejection of bubbles of diameter much smaller than the particle. Moderate evolution corresponded to greater quantity of somewhat more energetic bubbles which moved from the particle in a plume. Vigorous evolution was characterized by large bubbles of diameter comparable to the particle diameter; these left the particle individually with high velocity. The particle remained well-defined in the first two classes of evolution but was almost completely obscured by a vapor film and gas bubbles in the case of vigorous evolution. Thus, the first two cases appear to correspond to wetted particles, and vigorous evolution typifies nonwetted particles.

The increasing activity vs temperature, as illustrated in Fig. 2, was associated in each batch with a second characteristic termed the transition temperature. If the reactor temperature was raised after first exposure, particle activity increased. The increase in activity of particles in the slow and moderate classes was gradual and steady. However, within a temperature interval characteristic of each batch, moderate particles abruptly became vigorous. The interval over which this occurred was too narrow to be accompanied by a significant increase in hydrazine vapor pressure. This transition thus marks a change in degree of wetting, rather than a change in the rate of gas evolution. Below this transition temperature, particles are largely wetted and gas escapes from individual pores in small bubbles. Above the transition temperature there is essentially no wetting, with the particle surrounded by evolved gas; the gas formed within the gas film escapes as large bubbles.

Although a characteristic transition temperature was found for each batch of catalyst, the transition temperature is not exactly the same for all particles of one batch. The distribution of transition temperatures for the same catalyst tests reported in Fig. 2 is given in Fig. 3. While a relatively narrow temperature range encompasses most particles, it is clear that particles of varied characteristics are found in each sample. Even under uniform conditions, therefore, a particle-to-particle variation in wetting will result from the difference in intrinsic characteristics.

The final observation in each test was of particle breakup. Some particles broke upon first exposure; others broke upon heating, and some did not break. Breakup was always found to be associated with transition; particles which broke upon first exposure were also vigorous on first observation. In addition, all remnants of broken particles exhibited vigorous evolution.

Particles which were exposed at low initial temperatures were found to be more susceptible to breakup on reactor heating. Data from the same tests illustrated in Figs. 2 and 3 are listed in Table 1 and shown in Fig. 4. The fraction of particles breaking upon heating is high for low initial temperatures and decreases as the exposure temperature approaches the transition temperature.

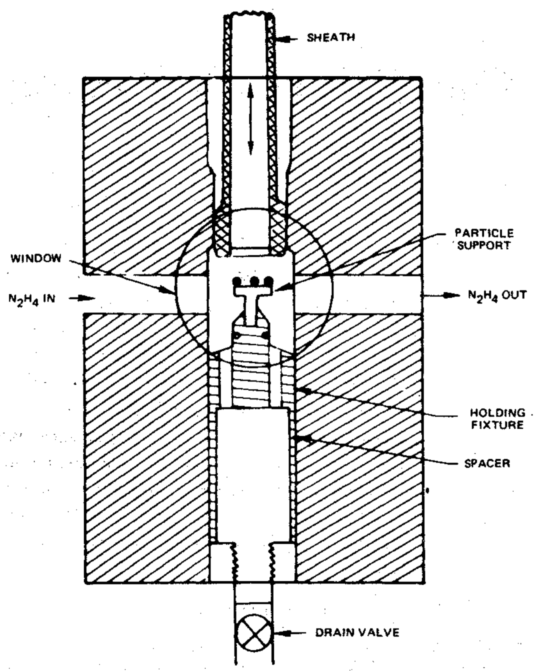

**Fig. 1 Effect of liquid temperature on initial activity of particle. Catalyst – lot 10-mem 20-30 mesh, as received.**

A logical picture of particle reactivity emerges from these observations. Particles which are very low in reactivity, although they may be extensively wetted, do not undergo a high rate of internal pressure buildup, because the rate of escape of gas from large pores is adequate to minimize internal forces. The very reactive particles generate gas near the surface rapidly enough to prevent wetting. In this instance, the internal pressure also does not rise. In intermediate cases, however, partial wetting can cause the rate of evolution of gases to exceed the rate of escape and the internal forces can build, causing breakup. When particles break, the newly exposed surfaces do not wet since the internally-tapped gases provide a vapor film, and the vigorous type of evolution results.

The important effect of initial temperature on breakup arises from the probability of wetting in discrete areas, rather than uniformly. At lower initial temperatures, a greater fraction of the surface will be wet since fewer areas of the particle can generate gas rapidly enough to prevent capillary intrusion. As the temperature is raised, however, the blocked pores tend to remain blocked until high internal pressures are attained.

The results of further tests on this and other catalyst batches are summarized in Table 2. The sum of the results indicates that each batch of catalyst has an essentially unique transition temperature and a specific rate of breakage which reflects a balance in the particle activity and strength. An important conclusion from those results is that an active particle could, in principle, be broken if initial wetting were sufficiently complete to block gas escape as the liquid temperature rose. An unexpected result is illustrated by Table 2. Both transition temperature and breakage are found to increase with decreasing particle size. That is, smaller particles are more readily wet and are more susceptible to breakage. Although the relationship between activity and breakage is consistent in all as-received samples, no clear reason for the trend has been apparent.

**Table 1 Summary of flow reactor results**[a]

| Initial reactor temp., °F | No. runs | Initial evolution | Breakup | | Transition range | Temperature average |
|---|---|---|---|---|---|---|
| | | | Initial | Upon heating | | |
| 31 | 18 | 18-slow | 0 | 14 | 50-83 | 65 |
| 35 | 22 | 21-slow | 0 | 11 | 60-80 | 71 |
| | | 1-moderate | 0 | 1 | 60 | 60 |
| | | 0-vigorous | 0 | 0 | – | – |
| 41 | 27 | 21-slow | 0 | 9 | 43-90 | 73 |
| | | 4-moderate | 0 | 3 | 60-90 | 73 |
| | | 2-vigorous | 1 | 0 | – | 41 |
| 51 | 17 | 2-slow | 0 | 1 | 70-75 | 73 |
| | | 13-moderate | 0 | 7 | 60-85 | 73 |
| | | 2-vigorous | 1 | 0 | – | 51 |
| 61 | 25 | 1-slow | 0 | 0 | 74 | 74 |
| | | 19-moderate | 0 | 5 | 62-85 | 74 |
| | | 5-vigorous | 0 | 0 | – | 61 |
| 71 | 17 | 0-slow | 0 | 0 | – | – |
| | | 11-moderate | 0 | 0 | 72-85 | 75 |
| | | 6-vigorous | 0 | 0 | – | 71 |
| 81 | 12 | 1-slow | 0 | 1 | 90 | 90 |
| | | 0-moderate | 0 | 1 | 90 | 90 |
| | | 0-moderate | 0 | 0 | – | – |
| | | 11-vigorous | 0 | 0 | – | 81 |

[a] Catalyst 20-30 Mesh Shell 405, Lot 10-MEM as-received, Hydrazine-Mil Spec, velocity 8 fps.

**Table 2 Catalyst particle transition temperature and breakup**

| Catalyst sample | Initial reactor temperature, °F | Average transition temperature, °F | Number (fraction) breaking | |
|---|---|---|---|---|
| 8-12 Mesh | | | | |
| Lot 4-MEM (as-received) | 32 | 32 | 0/27 | (0) |
| 14-18 Mesh | | | | |
| Lot 12-MEM (as-received) | 41 | 42 | 4/33 | (0.12) |
| Lot 6-LEM (as-received) | 32 | 32 | 0/9 | (0) |
| AFRPK L ≈ 25 (engine-fired) | 41 | 62 | 20/27 | (0.86) |
| 20-30 Mesh | | | | |
| Lot 10-MEM (as-received) | 41 | 63 | 27/48 | (0.56) |
| Lot 10526 (as-received) | 41 | 63 | 2/15 | (0.13) |
| AFRPL U ≈ 30 (engine-fired) | 61 | 92 | 6/48 | (0.13) |

The results of tests on engine-fired samples forwarded by AFRPL[2] are also given in Table 2. A 14-18 mesh sample (L ≈ 25),[‡] when tested at 71°F, resembled as-received 14-18 mesh samples at approximately 37°F. That is, there was moderate range of initial activities accompanied by significant breakage upon heating. It would appear that the engine-fired catalyst has suffered a significant reduction in activity, i.e., a higher reaction temperature is required for equivalent gas evolution. This could account for greater breakage at equal initial temperatures by virtue of much greater initial wetting. A factor which may co-exist is weakening of the substrate by other mechanisms.

Differences in activity were also noted between as-received 20-30 mesh particles and engine-fired 20-30 mesh catalyst (U ≈ 30),[§] from an upper bed. However, a much smaller fraction of engine-fired 20-30 mesh particles broke upon heating even though the transition temperatures were very high. The contrast between AFRPL L ≈ 25 and U ≈ 30 samples may be due to differences in the balance of activity, physical characteristics and strength of particles. The possibility of liquid completely filling part of the porous structure of the apparently inactive U ≈ 30 particles and retarding breakup must be considered.

Several aspects of the engine-fired particles were distinctly different from previously-conducted tests. First, the bubbles of gas products appeared to be smaller than for as-received particles. Secondly, the transition from slow to vigorous conditions was less abrupt. Thirdly, the particles generally fractured by simple splitting rather than exploding in a burst of fragments. Finally, at the temperatures of 61° or 71°F, particles which were classified as initially vigorous included some which required a short induction period of approximately one sec or less.

The results on as-received and engine-fired particles indicate that factors beyond intrinsic activity are important. The pore sizes and pore size distributions play an important role in determining the degree of wetting, the magnitude of internal pressure rise, and the differential pressure stresses across pore walls. Changes in these particle characteristics can

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[‡] Notation used by AFRPL to disgnate lower-bed packing of 14-18 mesh catalyst.

[§] Notation used by AFRPL to designate upper-bed pacing of 20-30 mesh catalyst.

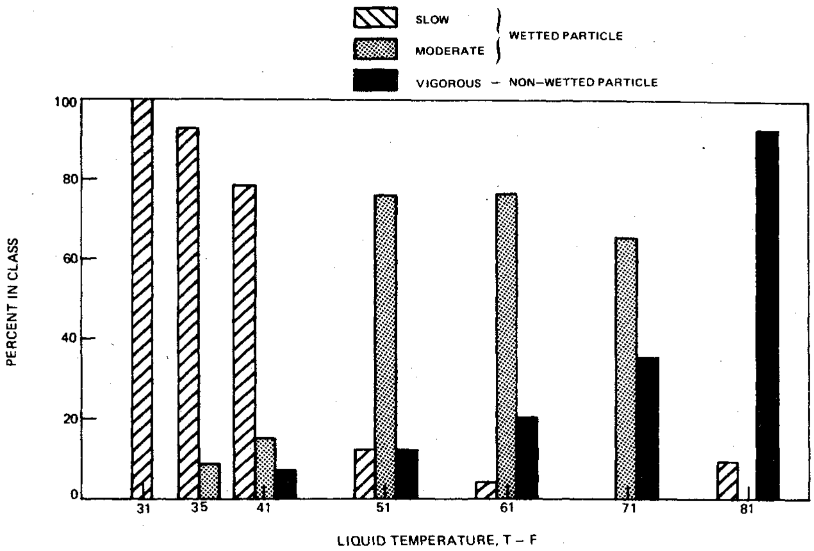

Fig. 2 Schematic diagram of reactor.

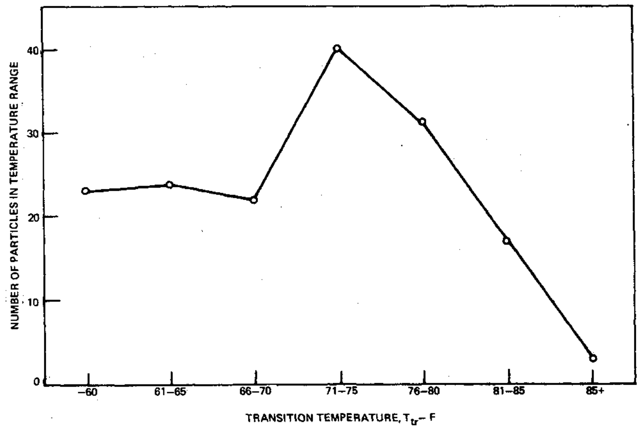

Fig. 3 Distribution of particle transition temperatures. Catalyst – lot 10-mem 20-30 mesh, as received.

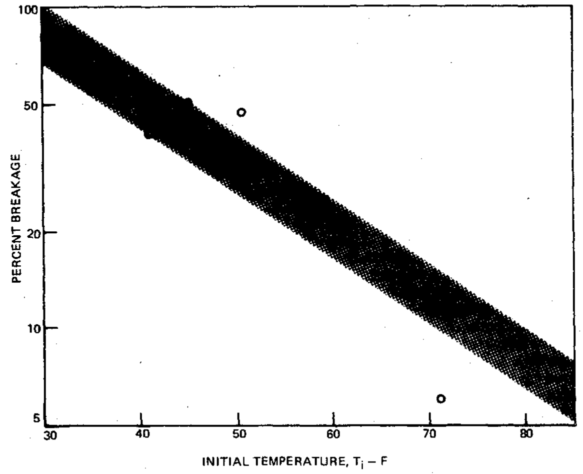

Fig. 4 Effect of hydrazine temperature on breakage upon heating. Catalyst – lot 10-mem 20-30 mesh, as received.

be induced by heating. Particles were subjected to a wide range of heating temperatures and times to determine the effect of heating on the relationship of wetting and breakup.

The results of heating as-received particles are detailed in Table 3. Particles of 14-18 and 20-30 mesh were heated in argon for times of one-half hour to overnight at temperatures of 375° to 1400°F. The effect of heating at 375°F for any period was to reduce breakage sharply with no change in activity. Heating at 500°F further reduced breakage with a small reduction in activity which was dependent upon heating time. Heating at 950°F or 1400°F for 2 hr or more caused severe reduction in activity and, as activity neared zero, resulted in zero breakup.

These results indicate that particle activity alone is not representative of breakage to be expected, since greatly reduced breakage is sometimes accompanied by only slight change in activity. The change in breakage cannot be ascribed to significant change in strength or pore characteristics, since only minor sintering would result from heating at 375° or 500°F. It would seem more likely that low temperature heating might affect the surface wettability.

Several parameters were found to have little effect on wetting or breakup in single particle tests. Flow velocity was found to affect the shape and velocity of the plume of evolved gases, but not the apparent rate of evolution. This reflects the fact that the capillary intrusion caused by surface tension involves pressures much greater than the dynamic pressure of the hydrazine stream. In packed-bed reactors, however, liquid velocity determines the penetration depth of liquid into the bed. Therefore, the total number of particles which may potentially be wet and break is dependent upon velocity.

Long immersion times at fixed temperature also had no effect on activity. Samples which were low in activity were left in place without heating as long as 1000 sec; no change in activity was found. However, if low activity particles were exposed to vapor by lowering the liquid, vigorous evolution was found after reimmersion. Lack of change in evolution under steady wetting is a result of continued heat transfer to the liquid; in the single particle tests the liquid temperature did not rise and evolution remained steady. However, lowering the liquid simultaneously removes the cooling effect of the liquid allowing increasing reaction rate as the particle heats, and reduces the internal pressure necessary to expel capillary liquid by removing the liquid. Once particle temperature and gaseous evolution are increased, reimmersion cannot quench reaction and vigorous evolution continues.

## Conclusions

The importance of wetting as a mechanism of catalyst particle breakup has been confirmed in this investigation. Important relationships between liquid temperature, catalyst reactivity, and catalyst wetting and breakup have been determined.

1) The strongest influence on wetting is the temperature of liquid hydrazine in which particles are immersed. For a given catalyst particle, reactivity increases markedly with temperature, since the liquid hydrazine vapor pressure is very sen-

Table 3 Transition temperatures and particle breakup in catalyst after heating in argon

| Sample, treatment | Transition temperature, °F | Number (fraction) breaking | |
|---|---|---|---|
| 14-18 Mesh | | | |
| Lot 12-MEM | | | |
| as-received | 42 | 4/33 | (0.12) |
| 2 hr, 500°F | 71 | 0/15 | (0) |
| 950°F | >110 | 1/12 | (0.08) |
| 1400°F | >110 | 0/12 | (0) |
| 20-30 Mesh | | | |
| Lot 10-MEM | | | |
| as-received | 63 | 27/48 | (0.56) |
| ½ hr, 375°F | 62 | 3/14 | (0.21) |
| 500°F | 69 | 1/15 | (0.07) |
| 1 hr, 375°F | 63 | 3/15 | (0.20) |
| 500°F | 67 | 1/15 | (0.07) |
| 1½ hr, 375°F | 62 | 3/15 | (0.20) |
| 500°F | 68 | 2/15 | (0.13) |
| 2 hr, 375°F | 63 | 4/16 | (0.25) |
| 500°F | 89 | 2/21 | (0.10) |
| 950°F | >110 | 2/12 | (0.16) |
| 1400°F | >110 | 0/12 | (0) |
| overnight, 375°F | 64 | 4/17 | (0.24) |
| 500°F | 97 | 2/15 | (0.13) |

sitive to temperature and it is the vapor which decomposes on the catalyst surface.

2) Immersion of particles at fixed temperature may result in either a wetted or a nonwetted state. Heating of the system produces spontaneous change to nonwetted conditions at a characteristic transition temperature.

3) Although an average transition temperature exists for each batch of catalyst, the transition temperature is not precisely the same for all particles, indicating that particles of varied characteristics are found in each sample.

4) Particles which were exposed at low initial temperatures were found to be more susceptible to breakup on reactor heating. This suggests that wetting is temperature-dependent with respect to both penetration depth and area.

5) The physical size of particles was found to be important. Both transition temperature and breakage were found to increase with decreasing particle size.

6) Low-temperature heating produced a surprisingly large and favorable effect on breakage. For heating conditions under which neither pore nor structural changes would be expected, reduction in breakage without change in activity was found. This suggests that changes in activity and breakup are not necessarily coupled, and that potentially important changes in one characteristic may be obtained without change in another.

## References

[1] Sangiovanni, J.J. and Kesten, A.S., "Motion Picture Studies of the Startup Characteristics of Liquid Hydrazine Catalytic Reactors," AIAA Paper, AIAA/SAE 7th Propulsion Joint Specialists Conference, 1971, pp. 71-102.

[2] Quirk J.A., "Hydrazine Engine Cold-Start Evaluation," CPIA Publication No. 260, Vol. I, Part II, *JANNAF Propulsion Meeting*, 1974, p. 447.