starch derivatives at D.S. 0.3 and 0.9 from 5% neutralized solutions and then dried and evaluated. Tear factor and wet breaking length were decreased, but bursting strength was increased about 50%, dry breaking length over 20%, and folding endurance was 2 to 3 times that of the uncoated paper.

DISCUSSION

High-amylose cornstarch was readily soluble in hot water when carboxymethylated (CM) to 1 substituent group per 10 anhydroglucose units (AGU); it was cold water-soluble at 2 or more CM groups per 10 AGU. The product exhibited typical polyelectrolyte properties, and its viscosity in solution was markedly reduced by salts. The viscosity was generally less than that of similar derivatives of ordinary starch or cellulose, but good stability was noted over the heating and cooling range of the Brabender Amylograph in both neutral and highly alkaline solutions. Some settling out of solution was noted, but setback was negligible.

Although unsatisfactory as a paper size, the carboxymethyl high-amylose starches had fairly good soil-suspending power. The inherent film-forming property of a high-amylose content material was displayed by the increase in tensile and bursting strength and in folding endurance of paper coated with this derivative.

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Density and Viscosity of Anhydrous Hydrazine at Elevated Temperatures

ROBERT C. AHLERT, GEORGE L. BAUERLE, and JOSEPH V. LECCE
Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, Calif.

THE VISCOSITY and density of hydrazine were determined experimentally from 288.16° and 296.24° K., respectively, to 449.83° K. The published data now cover a temperature range which extends into the autodecomposition region. Predictions of the density and viscosity of hydrazine, within 0.1% accuracy, may be made over the temperature range of the present investigation from correlations of the experimental data.

The advancement of hydrazine in recent years from the role of laboratory curiosity to a compound of increasing importance in the commercial and scientific world necessitated broadening of the temperature range over which the physical properties are known. The previously reported maximum temperatures at which the density and viscosity of hydrazine were known were 323.2° K. (*7*) and 344.3° K. (*6*), respectively.

This article presents the results of experimental measurements of the density and viscosity of hydrazine to temperatures extending into the autodecomposition region. A very careful application of standard laboratory methods enabled measurements of high accuracy. All experimental work was done in a completely inert atmosphere, to minimize the alteration of hydrazine purity by absorption of water and reaction with oxygen or carbon dioxide.

EXPERIMENTAL

Hydrazine used was of a purity greater than 99.6% by weight. The hydrazine used in the density determinations at 310.26° and 338.73° K. was of 99.9% purity at the start of the series, but picked up sufficient water to reduce purity to 99.6%. This sample had been prepared by stirring commercial-grade (about 97%) hydrazine over barium oxide for several hours, vacuum distilling, and twice passing the condensate through a packed column of Linde Molecular Sieves, Type 5A. Hydrazine used in the remainder of the density determinations and in all viscosity determinations was of 99.8% purity; pre- and posttest analyses showed no changes throughout the remainder of the experimental program. This sample was prepared by double distillation, under vacuum, of a barium oxide–hydrazine slurry. Oxide and hydrazine had been agitated under an inert atmosphere for about one day prior to the first distillation.

Analyses of hydrazine were performed in several steps. The hydrazine content of each sample was determined by the iodate titration method reported by Audrieth and Ogg (*1*), with a slight modification. The sample was enclosed in a dissolvable gelatin capsule to minimize atmospheric contamination and vapor loss. This method permits hydrazine assays to ±0.1%. Impurities, chiefly water and ammonia, were determined by chromatographic techniques.

Density determinations were made with sealed borosilicate glass pycnometers, of approximately 2-ml. capacity, with precision bore capillary tubing attached to spherical bulbs. Reference marks were etched on the capillary stem at frequent intervals, to facilitate liquid level measurements. The pycnometers were calibrated over the range of temperatures for which the density of hydrazine was desired. Fluids used for calibrating were water or mercury, depending on the temperature of calibration.

Hydrazine was introduced into the pycnometer under an atmosphere of nitrogen. The pycnometer was capped, weighed, sealed permanently, placed in the constant temperature bath, and heated to a preselected temperature. After thermal equilibrium was attained, a cathetometer was employed to measure liquid level in the capillary stem and, hence, the volume of hydrazine. Density was calculated from the weight and volume of hydrazine, with corrections made to account for the effects of inert gas, vapor, and buoyancy. Displacements of 0.001 mm. were measurable with the cathetometer.

A constant temperature bath, which featured a plate-glass viewing window, was constructed for this study. Parallax was avoided by use of the flat, plate-glass window. Diatomaceous earth insulation was sandwiched between double walls at the sides, back, and bottom of the temperature bath.

Heaters of various sizes furnished coarse and fine adjustment of the fluid temperature. A mercury thermoregulator and electronic relay circuitry provided control within ±0.02° K. of the desired temperature. Precision platinum resistance thermometers, certified by the National Bureau of Standards, provided temperature measurement of an equivalent accuracy. Traverses of the bath, in the region of the controller and pycnometer and/or viscometer, with the resistance thermometers revealed no measurable variation of temperature around the control value.

Viscosity measurements were made with modified Zhukov viscometers. This design permitted a small sample, ensured constancy of sample volume, allowed the sample to remain in the bulb reservoir until thermal equilibrium was attained, and could be sealed conveniently. Viscometers were calibrated with fluids of known kinematic viscosity at each temperature. The calibrants were water and National Bureau of Standards certified test oils, Types D and I. The calibrating technique involved timing the flow of the two fluids and calculation of the constants, *B* and *C*, in the equation:

$$\eta/\rho = Ct + B/t \qquad (1)$$

where t is time of flow, seconds, η is absolute viscosity, centipoises, and ρ is density, grams per cubic centimeter.

RESULTS AND DISCUSSION

Table I presents density data reported by several investigators. The experimental values of this study are given in Table II. The data appear in good agreement, indicating that the purity of hydrazine was relatively consistent. Least square fits of the data of the present investigation and of the present data with those presented in Table I were carried out. The combined data, because of the greater number of points of approximately the same precision, correlated with a smaller standard deviation. The equation:

$$\rho = 1.2471 - 0.07226\,(T/100) - 0.003191\,(T/100)^2 \qquad (2)$$

where ρ is density in grams per cubic centimeter, and T is temperature in degrees Kelvin, empirically represents all data with a standard deviation of 0.0006 gram per cc. Predictions of density for anhydrous hydrazine may be made with this equation, to within ±0.0002 gram per cc., with 95% reliability.

Table I. Published Density Values of Hydrazine

Temp., ° K.	Density, G./Cc.	Source	Temp., ° K.	Density, G./Cc.	Source
273.2	1.0258	(*3*)	298.2	1.0045	(*8*)
273.2	1.0253	(*8*)	298.2	1.0036	(*8*)
288.2	1.0131	(*5*)	298.2	1.0024	(*7*)
293.2	1.0085	(*3*)	308.2	0.9955	(*2*)
295.5	1.0065	(*3*)	323.2	0.9801	(*7*)

Table II. Density of Hydrazine

(Experimental values)

Temp., ° K.	Density, G./Cc.	Temp., ° K.	Density, G./Cc.	Temp., ° K.	Density, G./Cc.
296.24	1.0059	338.73	0.9672	394.27	0.9124
299.75	1.0026	338.73	0.9672	394.27	0.9124
310.26	0.9942	338.73	0.9671	422.05	0.8862
310.26	0.9946	366.49	0.9388	422.04	0.8863
310.26	0.9930	366.49	0.9398	449.83	0.8573
310.26	0.9931	366.49	0.9391	449.83	0.8577

Based on ideal gas considerations, pycnometer pressures were estimated to have reached 12 atm. at 449.83° K. However, appreciable decomposition occurred after 15 minutes at this temperature. Therefore, this estimate of maximum pressure was believed to be conservative.

Table III presents the viscosity data of Walden and Hilgert (*8*), Semishin (*7*), and Mason (*6*); Table IV presents the data of the present investigation. Experimental results are reported in kinematic units, centistokes, the directly calculated quantity (Equation 1). Absolute viscosities, incorporating the density data of Equation 2, are given in this table also. An extrapolation of Equation 2 was used to calculate the absolute viscosity at 288.16° K. The present data and the published data agree fairly well, but there is some scatter.

Table III. Published Viscosity Values of Hydrazine

Temp., ° K.	Viscosity, Cp.	Source	Temp., ° K.	Viscosity, Cp.	Source
274.2	1.293	(*8*)	288.2	1.044	(*8*)
275.2	1.272	(*8*)	293.2	0.9736	(*8*)
276.2	1.251	(*8*)	298.2	0.9049	(*8*)
277.6	1.347	(*6*)	298.2	0.9031	(*7*)
278.2	1.207	(*8*)	311.0	0.754	(*6*)
283.2	1.118	(*8*)	323.2	0.6731	(*7*)
			344.3	0.504	(*6*)

Inaccuracies in viscosity determinations are assignable to several sources. These include: gaseous evolution by either homogeneous or heterogeneous decomposition, uncorrected capillary end effects, and purity of sample.

End effects normally cause driving pseudo-pressures to be somewhat lower than in ideal flow, resulting in excessive flow times and apparent high viscosities. These end effects become more pronounced at higher velocities. Gaseous evolution will also cause excessive flow times and high viscosities.

A high degree of hydrate formation and association will cause mixtures of hydrazine and small amounts of water to exhibit higher viscosities than pure hydrazine. The value of the kinematic viscosity, which is the experimentally determined quantity, will depend on the proportional increase in density also. Semishin (*7*) and Dito (*4*) showed that the addition of water will cause an increase in density. It is likely that the viscosity increase is proportionally larger than the density increase, resulting in slightly larger kinematic viscosities.

Table IV. Viscosity of Hydrazine

(Experimental values)

Temp., ° K.	Kinematic Viscosity, Cs.	Absolute Viscosity, Cp.
288.16	1.0159	1.0225
310.94	0.7316	0.7268
338.72	0.5399	0.5363
366.49	0.4286	0.4028
394.27	0.3578	0.3266
422.05	0.3081	0.2728
449.83	0.2733	0.2344

In the region of overlap of present and reported data, decomposition is negligible and it is unlikely that sufficient water could have been absorbed to cause the deviation in data. The scatter of viscosity data appears to be assignable only to differences in technique and to the handling of end-effect corrections. The results of the present investigation appear to be generally lower, indicating that (if end losses cause high flow times and, consequently, high measured viscosities) a more complete correction of end effects was made in this study.

Correlations were again attempted of the present data and of the combination of published and present data. Because of the slight scatter of the complete set of data, the combined correlation was not as good as that of the present data only. A least square fit of the data of this study is represented by the equation:

$$\ln(\eta/\rho) = -2.4830 + \frac{404.28}{(T)} + \frac{26.197\,(10)^6}{(T)^3} \qquad (3)$$

where (η/ρ) is kinematic viscosity, centistokes, and T is temperature, ° K. The equation represents the data with a standard deviation of 0.0013 in log space, corresponding to ±0.0013 cs. at the lower temperatures. It may be used to predict the viscosity of hydrazine to within 0.10% with 95% confidence. This corresponds to actual kinematic viscosity predictions of ±0.0010 cs. at the lower temperatures. The slight curvature in log space indicates that an Arrhenius-type representation is not strictly applicable.

Experimental errors of ±0.0002 gram per cc. and ±0.0014 cs. for density and viscosity, respectively, were predicted for these investigations, on the basis of the theory of propagation of errors. Actual density determinations showed a standard deviation of 0.0007 gram per cc. Slight experimental nonuniformities can cause errors of this magnitude. Latter tests, as shown by the data, indicate that the experimental technique had improved and reduced the error to within the predicted 0.0002 gram per cc. The deviation in viscosity determinations—i.e., ±0.0013 cs. at the lower temperatures—was almost exactly the predicted value of ±0.0014 cs.

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NOMENCLATURE

η = absolute viscosity, cp.
ρ = density, g./cc.
B = viscometer constant
C = viscometer constant
t = time, seconds
T = temperature, ° K.

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