

# Testing the structure of magnetic paints with and without superimposed shear

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## Synopsis

The structure development in dispersions of magnetic barium ferrite particles in cyclohexanone with polyvinylchloride wetting resin was tested by oscillatory rheological measurements and orthogonal superposition of steady and oscillatory shear. The optimum dispersion is achieved at the resin concentration  $c = c_0$ , which corresponds to a minimum in the viscoelastic moduli. At  $c < c_0$  the system is highly elastic, brittle ( $G'$  drops sharply and  $G''$  goes through a strong maximum at high strain), thixotropic and its relaxation spectrum,  $H(\tau)$ , is dominated by long relaxation times,  $\tau$ , which indicates the existence of a strong network. At  $c > c_0$  the system becomes less elastic, more flexible, less thixotropic and  $H(\tau)$  is dominated by short  $\tau$ , which indicates that the structure formation in this case is dominated by small aggregates rather than a network. By superimposing steady and oscillatory shear we show that the steady shear dramatically break the structure and shifts  $H(\tau)$  to very short  $\tau$ . © 1997 The Society of Rheology. [S0148-6055(97)00806-7]

## I. INTRODUCTION

Rheological measurements are widely used to probe the structure of dispersions. Steady shear viscosity characterizes the shear-induced breakup of aggregates [Firth and Hunter (1976), Patel and Russel (1988), De Rooij *et al.* (1993)]. Small amplitude oscillatory rheometry is a well known tool to test the viscoelasticity of the networklike structures developed in the dispersions [see e.g., Kanai *et al.* (1992), De Rooij *et al.* (1994), Potanin *et al.* (1994)]. Oscillatory measurements are in principle more informative since they test the structure at different timescales. However, until recently they were applied only to test the structure developed at rest. The well understood necessity to develop methods for probing the viscoelasticity of shear-controlled structures lead rheologists to design rheometers in which small amplitude oscillations are superimposed on the steady

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shear flow. Both parallel [Van den Ende *et al.* (1992)] and orthogonal [Zeegers *et al.* (1995)] superposition were implemented. Zeegers *et al.* (1995) pointed out that the orthogonal superposition dynamic viscometer (OSDV) is more effective at low frequencies and in many ways easier to interpret.

In this paper we will use the OSDV along with a conventional rheometer to test the structure of dispersions of magnetic particles. These dispersions are used for production of magnetic coatings (e.g., for videotapes). They include three main components: magnetic pigment particles, resins, and solvents. Pigment particles are either elongated (acicular), such as particles of iron oxide, or platelets, such as particles of barium ferrite [Orii *et al.* (1991), Inoue *et al.* (1993), Kudo *et al.* (1994)]. The resin maintains durable, flexible coating that adheres to the substrate upon crosslinking [O'Grady *et al.* (1991)]. Recently attention has been focused on the use of "wetting resins" which also play the role of a dispersing agent. Due to strong magnetic forces the pigment particles are combined into small *primary aggregates* which are not separated by milling or high shear [Scholten *et al.* (1990)]. They build reversible viscoelastic networks, as confirmed by rheological measurements [Kanai *et al.* (1992)].

## II. MATERIALS AND METHODS

We have studied a model system composed of barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) particles, wetting resin and the low volatility commercial solvent, cyclohexanone. The polyvinylchloride wetting resin (averaged molecular weight 26 000) was supplied by Nippon Zeon Co. It includes 0.7 wt. %  $\text{SO}_4$ , 0.6 wt. % OH groups and 3.0 wt. % epoxy content. Jeon *et al.* (1997) have shown that the resin is adsorbed by oxide particles through both basic and acidic sites. The resin dissolves completely in cyclohexanone, producing a transparent solution. The barium ferrite pigment particles (HEX- $\Sigma$ T50130 from TODA KOGYO Corp.) are hexagonal platelets 30 nm in diameter and specific surface area  $51 \text{ m}^2/\text{g}$ . They have coercivity 1300 Oe and specific magnetic moment  $57.5 \text{ emu/g}$ . Mixing the pigment, solvent and resin and subsequent milling in an Eiger Mini 50 cc bead mill produced a visually homogeneous paint. In our experiments we found out that after about 30 min of milling (the actual time slightly varies with composition) an equilibrium was achieved so that rheological properties of the paint remained constant during further milling (for at least 4 h). All our experiments were performed on samples in which such an equilibrium was achieved.

The experiments were performed at different *resin concentrations*,  $c$ , which is defined as the weight concentration of the resin in the initial pure solution before the pigment is added. We also define the *pigment concentration* or volume fraction,  $\phi$ , as the volume fraction of the pigment particles in the paint, the pure resin solution of concentration  $c$  being a medium for these particles.

Some insight into the structure of the paint is provided by cryo-TEM (transmission electron microscopy) of the frozen paint samples. The images of the paint at different resin concentration were published by Potanin *et al.* (1997). The particles seem somewhat better dispersed at higher  $c$ . However, such TEM images give mostly qualitative information about the structure. For a quantitative characterization, rheological measurements were used.

A HAAKE RS-100 controlled shear stress rotational rheometer was used for dynamic measurements with cone-plate (35 mm,  $4^\circ$  angle) geometry. To measure viscoelastic moduli with steady shear the OSDV with double gap geometry was used. It was built by the Rheology Group at Twente University and is described by Zeegers *et al.* (1995). The annular cup can be rotated axially which creates a steady shear flow with the shear rate  $\dot{\gamma}$

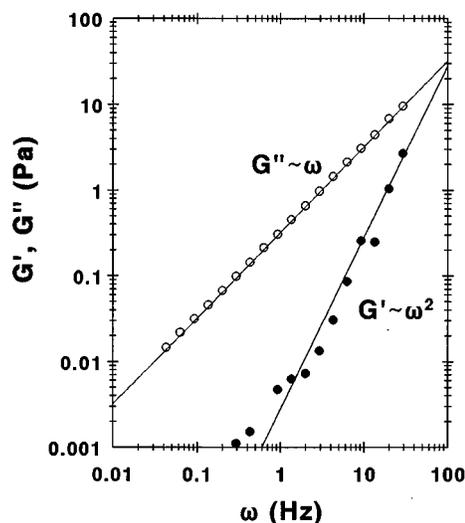


FIG. 1. Viscoelastic moduli vs the angular frequency,  $\omega$ , of resin solution at  $c = 20\%$  (no pigment).

between the measuring cylinder and the cup. The small amplitude harmonic oscillation in the vertical direction is driven by an excitator with adjustable angular frequency  $\omega$ . The vertical displacement is measured and the moduli,  $G'$  and  $G''$ , are calculated from the measurements as functions of  $\omega$  and  $\dot{\gamma}$ . All measurements were performed at temperature 20 °C.

### III. EXPERIMENTAL MEASUREMENTS

Figure 1 shows the storage modulus,  $G'$ , and the loss modulus,  $G''$ , of the pure resin solution at  $c = 20\%$ . The moduli lie in the terminal zone, i.e.,  $G' \sim \omega^2$ ,  $G' \ll G'' \sim \omega$ . All experiments described below were performed at  $c \leq 20\%$ . Hence, up to the highest  $c$  studied in this work the polymer coils are fully relaxed, non-entangled, and the pure resin solution is a viscous fluid with negligible elasticity and constant viscosity,  $\mu_0 \equiv G''/\omega$ .

The pigment particles build a viscoelastic network in the paint with the moduli,  $G'$  and  $G''$ , being several orders of magnitude higher than those of a pure resin solution. At low stresses the network responds linearly, while at higher stresses the network is broken. Rupture of the network results in a sharp decrease of the storage modulus and a maximum for the loss modulus is observed (Fig. 2). All measurements reported below were performed in the linear regime.

Figure 3 shows the viscoelastic moduli versus  $c$ . Both  $G'$  and  $G''$  go through their minimum values at  $c = c_0 \approx 5\%$ . For comparison we also plotted the  $G''$  for the pure resin solution, which in the terminal zone is identical to  $\mu_0\omega$ . For the pure resin solution  $G' \ll G''$  (cf. Fig. 1), whereas for the paint  $G' \gg G''$ .

It is easy to notice a qualitative change in the frequency dependencies of the viscoelastic moduli in Fig. 4. At low  $c$  not only the absolute values of  $G'$  and  $G''$  are high, but the shape of the curves, especially of the  $G''(\omega)$ , indicate the existence of a strong

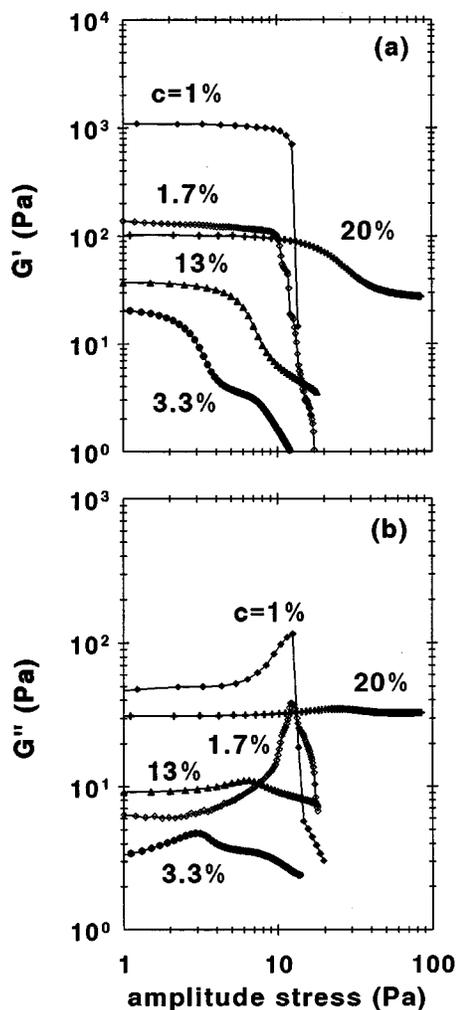


FIG. 2. (a)  $G'$  and (b)  $G''$  are plotted against the deformation stress amplitude at a frequency 1 Hz,  $\phi = 6.5\%$  and different  $c$ .

large-scale structure contributing at low frequencies. On the contrary, at high  $c$  the response is dominated by small-scale structure contributing at high frequencies.

Another interesting insight into the development of the structures at various  $c$  is provided by the after-shear recovery experiments. In Fig. 5 we plot  $G'$  during the recovery after subjecting a sample to the high-shear deformation at shear rate  $100 \text{ s}^{-1}$  for 1 min. Low  $c$  samples recover much slower indicating the development of a networklike structure.

Figure 6 shows the effect of superimposed shear. Shear breaks down the network structure which results in a significant decrease of  $G'$  at low frequencies. The effect of shear on  $G''$  is more complicated. Low-frequency values of  $G''$  decrease with shear rate,  $\dot{\gamma}$ , but at high frequencies  $G''$  increases with  $\dot{\gamma}$ . Both, resin (at low  $c$ ) and shear, decrease

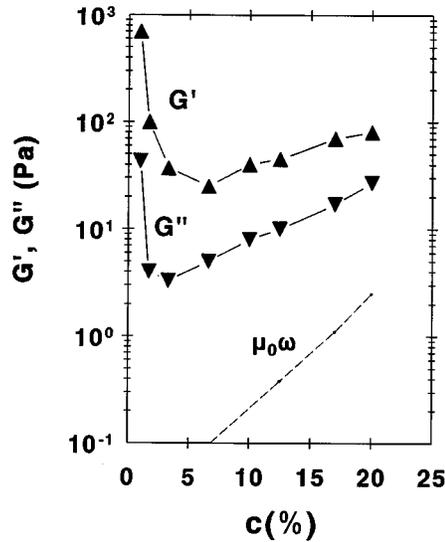


FIG. 3. Viscoelastic moduli vs  $c$  at  $\phi = 6.5\%$  and a frequency 1 Hz.

the contribution to the moduli at low frequencies which indicates that they both break down the network structure. At high  $c$  the moduli slightly increase with  $c$ .

#### IV. DISCUSSION

From our experiments we distinguish between two types of structure transformations in the paint: the resin-induced and the shear-induced. Comparing Figs. 4 and 6 we see a decrease of low- $\omega$  contribution to the moduli with growth of  $c$  and  $\dot{\gamma}$  which should be attributed to a weakening of the network structure in the paint due to the adsorption of the resin (resin-induced mechanism), and due to shear (shear-induced mechanism), respectively. The resin-induced mechanism is effective at low enough  $c$  (above  $c = 13\%$  the moduli in Fig. 4 grow in the entire  $\omega$  range). A somewhat more compact way to present the same results is to plot the relaxation spectrum,  $H(\tau)$ , against the relaxation time,  $\tau$ . The spectrum is defined by [Böhme (1991)]:

$$G' \equiv \int_0^{\infty} \frac{d\tau}{\tau} H(\tau) \frac{(\omega\tau)^2}{1+(\omega\tau)^2}, \quad G'' \equiv \int_0^{\infty} \frac{d\tau}{\tau} H(\tau) \frac{\omega\tau}{1+(\omega\tau)^2}. \quad (1)$$

The spectra are shown in Figs. 7 and 8. They were calculated from  $G'(\omega)$  and  $G''(\omega)$  by solving numerically the integral equations (1) using the regularization algorithm NLREG [Weese (1993)] supplied by HAAKE. As  $c$  increases the long- $\tau$  part of  $H(\tau)$ , which is responsible for the low-frequency moduli, decreases and the short- $\tau$  part increases. Since the long- $\tau$  part represents a contribution from the long-scale structure, this change of  $H(\tau)$  should be interpreted as a transition from the networklike structure to a system of weakly interacting primary aggregates. However, at  $c > c_0 \approx 5\%$  adding more resin doesn't help to disperse the pigment any better. Even the long- $\tau$  part of  $H(\tau)$  starts to grow. The shear-induced breakdown is more effective. Figure 8 shows that applying shear we achieve further reduction in the long- $\tau$  part of  $H(\tau)$ .

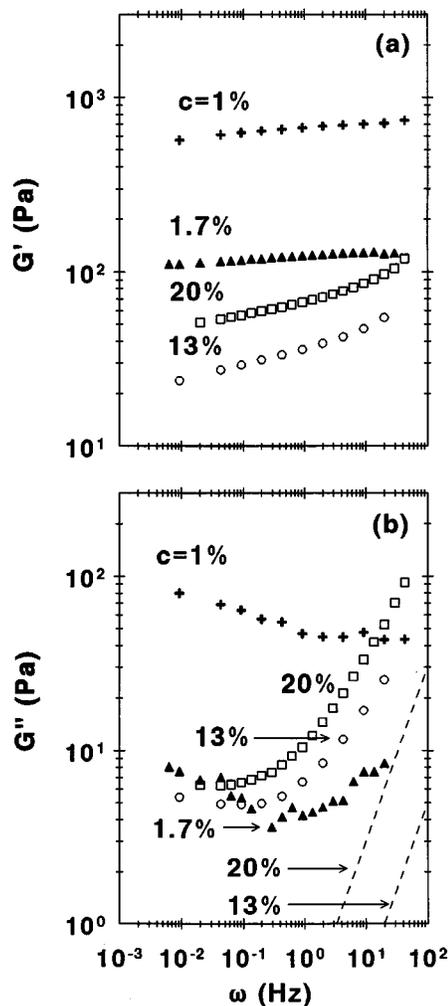


FIG. 4. (a)  $G'$  and (b)  $G''$  vs angular frequency at  $\phi = 6.5\%$  and different  $c$ . Dashed lines on (b) show  $G''$  of resin solution at different  $c$ .

The resin-induced structural changes are demonstrated by several other experiments. Figure 2 shows that as  $c$  increases, the network becomes less brittle: the decrease of  $G'$  due to the breakdown of the structure becomes less sharp and the corresponding peak of  $G''$  is lowered and completely disappears at  $c = 20\%$ . In Fig. 9 we plot the critical strain,  $\gamma_{cr}$ , defined as the amplitude strain which corresponds to the decrease of  $|G|$  by a factor of 2. The strong increase of  $\gamma_{cr}$  with  $c$  indicates the increase of flexibility of the structure with the addition of the resin. Again, this can be interpreted as a transition from a strong networklike structure at low  $c$  to a system of weakly interacting primary aggregates at high  $c$ . The former is responsible for high elasticity at small strains, but is easily broken at large strains. The latter is less elastic, but more flexible at high strains.

Increased flexibility of the structure at high  $c$  can also be due to the change of the interactions between primary aggregates. As  $c$  is increased the primary aggregates be-

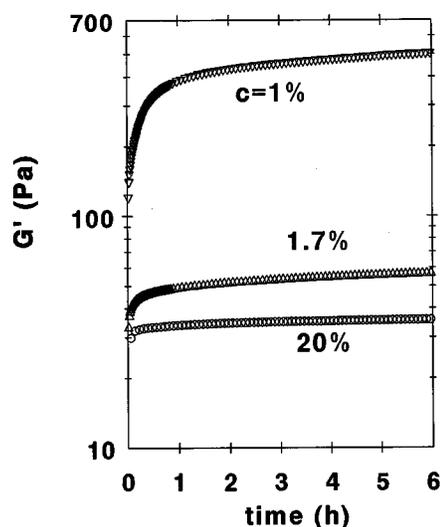


FIG. 5.  $G'$  is shown vs time after a preshear at  $100 \text{ s}^{-1}$  applied for 1 min at  $\phi = 6.5\%$  and a frequency 1 Hz.

come better separated due to the buildup of adsorption layers. In actuality, both processes probably interfere in making the structure more flexible at high  $c$ , i.e., the range of interactions is increased due to higher adsorption and the length scale of the structure is decreased due to better dispersion.

The conclusion that the structure of the paint is changed from predominantly network to predominantly aggregates is also demonstrated by the recovery experiments shown in Fig. 5. At high  $c$  the after-shear recovery is quick because small aggregates quickly regain their shape only slightly perturbed by shear. Recovery of the large-scale network structure takes longer and results in a stronger increase of  $G'$ , i.e., the low- $c$  samples are more thixotropic.

At high  $c$  the moduli start to increase with the addition of extra resin as shown in Fig. 3. This can be attributed to the depletion flocculation. Indeed, Jeon *et al.* (1997), have studied adsorption of the same polyvinyl chloride (PVC) binder on oxide surfaces. They have shown that at high  $c$  adsorption saturates, i.e., free resin is accumulated in the system which may lead to depletion flocculation of primary aggregates. The effect has been widely studied [Prestidge and Tadros (1988)] and it is known that the accumulation of the extra free resin results in viscosity going through a minimum at a certain resin concentration [Zaman *et al.* (1996)].

Alternative possible explanation is bridging between particles by resin molecules. However, low averaged molecular weight of the resin ( $M_w = 26\,000$ ) implies that bridging can only occur through the longest molecules in this polydisperse resin.

Another interesting phenomena shown by Fig. 2 is the emergence of an intermediate plateau of  $G'$  at certain stress amplitude at  $c > 3\%$ . This can be an indication of a two-level "nested" structure formation with a strong but flexible super-structure which builds up at high  $c$ . Alternatively, this intermediate plateau can be attributed to the structural rearrangements which take place at high strains. The latter explanation was

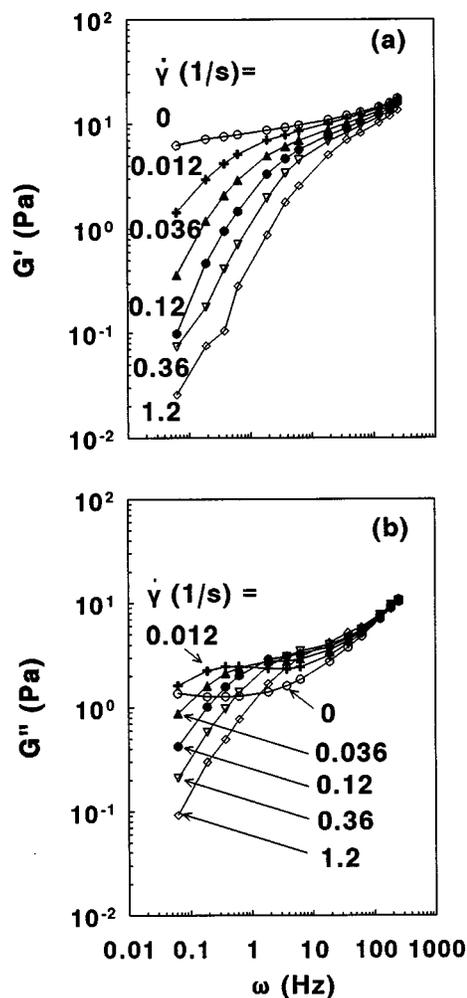


FIG. 6. (a)  $G'$  and (b)  $G''$  vs angular frequency at  $\phi = 5\%$ ,  $c = 3.3\%$  and different superimposed shear rates,  $\dot{\gamma}$ .

proposed by Kanai and Amari (1993) who studied the strain-thickening behavior of iron oxide dispersions. They attributed the rise of moduli at high strains to the loosening of flocs. As distinct from them we don't see the actual *increase* of moduli at high strains, but the emergence of the high-strain plateau can be due to a similar phenomena. Kanai and Amari have shown that the strain-thickening is stronger for better dispersed systems (nonmagnetic oxides in their case). This is consistent with the fact that we see our plateau only at high  $c$ , in which case the primary aggregates are better separated and therefore easier to rearrange.

## V. CONCLUSION

We have compared the resin- and the shear-induced structural transformations in the magnetic paints. At low resin concentration the resin-induced breakdown of the large-

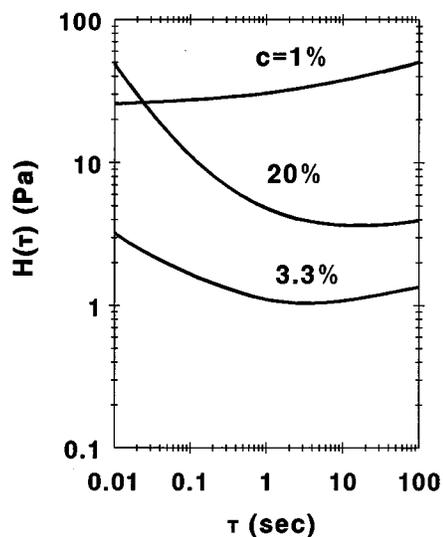


FIG. 7. Relaxation spectrum,  $H(\tau)$ , calculated from the viscoelastic moduli, vs  $\tau$  at  $\phi = 6.5\%$  and different  $c$ .

scale network structure is similar to the shear-induced breakdown: in both cases the relaxation spectrum is shifted to shorter times indicating the transition to smaller scale aggregates. At high resin concentration the viscoelastic moduli increase, possibly, due to depletion flocculation effect or bridging between particles by the resin.

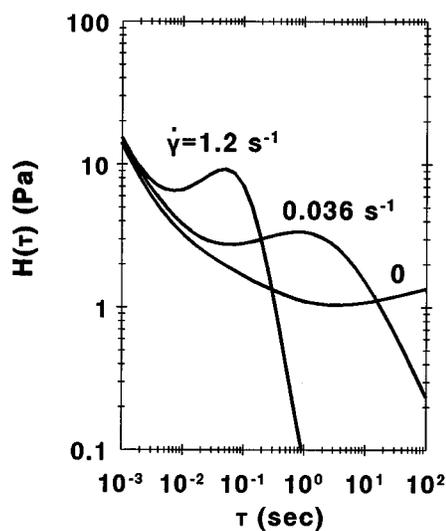


FIG. 8. Relaxation spectrum,  $H(\tau)$ , calculated from the viscoelastic moduli, vs  $\tau$  at  $\phi = 6.5\%$ ,  $c = 3.3\%$  and different superimposed shear rates,  $\dot{\gamma}$ .

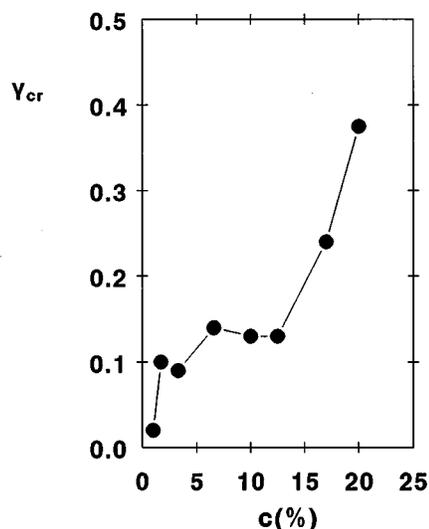


FIG. 9. Critical strain,  $\gamma_{cr}$ , which corresponds to the nonlinearity start in oscillatory measurements, is plotted against the resin concentration,  $c$ , at a frequency 1 Hz and  $\phi = 6.5\%$ .

## ACKNOWLEDGMENTS

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