A high-magnification, black and white micrograph showing a dense, granular, and somewhat fibrous structure, likely representing engine combustion deposits. The texture is complex, with many small, irregular particles and some larger, more rounded clumps. The overall appearance is that of a microscopic view of a solid material with a high degree of surface area and irregular morphology.

# CHEMISTRY OF ENGINE COMBUSTION DEPOSITS

EDITED BY  
LAWRENCE B. EBERT

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## PREFACE

On March 30, 1981, a symposium entitled "Chemistry of Engine Combustion Deposits" was held at the 181st American Chemical Society National Meeting in Atlanta, Georgia, under the sponsorship of the Petroleum Division. This book is an outgrowth of that symposium, including papers from all of the Atlanta presentors, as well as from others who were invited to contribute.

Research on engine deposits has not been as "glamorous" as in the related fossil fuel areas of petroleum, coal, or oil shale, and publications in the field have been largely confined to combustion and automotive engineering journals. One objective of this book is to bring a large body of work on the chemistry of deposits into more general accessibility. We hope to make people more familiar with what deposits are, with what problems they cause, and with what present workers are doing to solve these problems.

The creation of the book has involved many people. Patricia M. Vann of Plenum Publishing Corporation gave guidance in planning. We thank Claire Bromley, Ellen Gabriel, and Halina Markowski for the preparation of many of the Exxon contributions. Finally, we thank Joseph C. Scanlon for his useful advice and encouragement.

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## INTRODUCTION

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The symposium reported in this book was held in early 1981 and is based on work performed during the preceding few years when soaring fuel prices and impending shortages had stimulated studies of all factors affecting the efficiency of fuel use and manufacture. Deposits formed in the engine combustion chamber are of major interest because they affect engine efficiency by changing fuel octane number requirement and by changing heat loss to the cooling system. Physical interference with piston ring and gas flow through the valves can also occur. Also, the porous nature of the deposits is believed to be responsible for cyclic accumulation and release of hydrocarbons, thus increasing hydrocarbon emissions.

The papers, presented here, highlight the complex nature of sources of deposits and their effects on engine performance.

Recent changes in lubricant and fuel composition as well as engine design have forced re-evaluation of the nature of the problem, and the classic engine and fleet testing remain an important component of an overall program. Confirming older work, deposits in the end gas zone are held responsible for octane requirement increase. Both fuel and lubricant can contribute. Oil consumption is important since oil can contribute inorganic components and reactive molecules. The relative contribution of fuel and lubricant depends strongly on their composition and on engine design and condition. Inorganic fuel components are becoming less important with the drastic reduction in lead tetraethyl content, but the accompanying increase in aromatics tends to increase deposit formation. A new observation is the reported large increase in fuel economy resulting from reduced heat loss to



cooling water when the combustion chamber is insulated on the inside by combustion deposits or by a teflon coating. The implications of this observation obviously require further study since deposits in the end zone are probably deleterious because of ORI, while the insulating effect of deposits elsewhere may be desirable.

A highlight of the symposium is the application of modern analytical and computer modeling methods to advance toward a more detailed understanding of the chemistry and physics of deposits and their effect of ORI on performance. A computer model, taking into account the cyclic heat transfer through an insulating layer of deposit, shows the effect of increasing end gas temperature (and, therefore, knocking tendency), the effect of lowered heat loss on efficiency and the small effect of deposit volume on compression ratio. While in their early stages, such models are an important tool for quantitative testing of various hypotheses for explanation of observed effects.

Relatively little work has been done on the chemistry of the polymerization process by which deposits are formed. Studies of composition have, however, advanced by adding  $^{13}\text{C}$  NMR to the array of tools being applied to this problem. The bulk of carbon in deposits from both engines and a laboratory flame was found to be aromatic in nature. This correlates with the observation that aromatic compounds in fuel or lubricant greatly increase deposit formation. Studies using a laboratory laminar flame produced deposits from benzene fuel, but none from an aliphatic fuel. Formaldehyde and acetylene diffused to the cold surface for both flames; however, phenol was a major diffusing species for the deposit forming benzene and is implicated as a contributor to deposit formation.

Research on the spark ignition engine deposit problem has diminished with the current decrease in concern over fuel price and supply; however, the economic problem of continuing high cost for fuel to the consumer, and international competition for improved engine performance calls for continued effort to understand and solve deposit related problems.

## CHEMISTRY OF ENGINE COMBUSTION DEPOSITS: LITERATURE REVIEW

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### I. INTRODUCTION

As an automobile engine runs, its fuel quality requirements, as measured by the octane number of the fuel needed to inhibit knocking, may change in time. Historically, this phenomenon is referred to as the "ORI" problem, standing for octane requirement increase.

Octane requirement increase can be quantified. Knock can be perceived, by either people or instruments, by an audible "pinging" sound emanating from the engine, caused by an approximately 5000 Hz vibration of the engine structure induced by gas pressure waves within the combustion chamber. These waves are created by "auto ignition" of the gas ahead of the normal flame front. By using a variety of test fuels, of known octane rating, one determines the octane requirement of the engine as that octane for which knock is "borderline". The octane requirement increase is simply the difference between the final octane requirement and the initial octane requirement of an engine. Figure 1 illustrates actual examples of the "ORI" problem.

The single most important operational variable affecting "ORI" is the presence of combustion chamber deposits. As the flame front progresses across the chamber, it never actually touches the relatively cool wall, and carbonaceous materials coat the inside surfaces of the combustion volume, illustrated in Figure 2. Modification or elimination of these deposits can have a beneficial impact on the octane requirement increase problem.

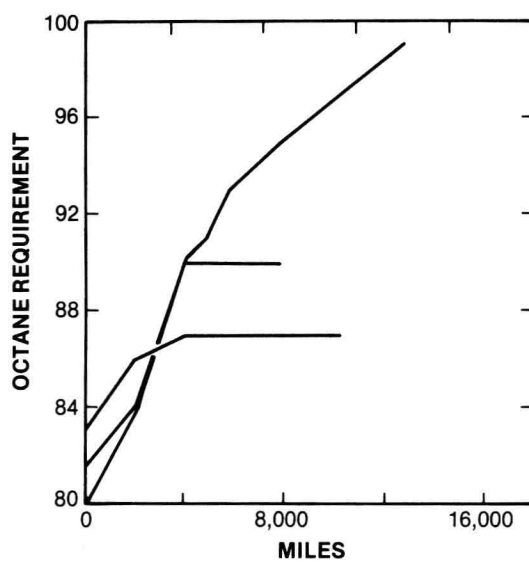


Figure 1. Examples of "octane requirement increase" for automobile engines.



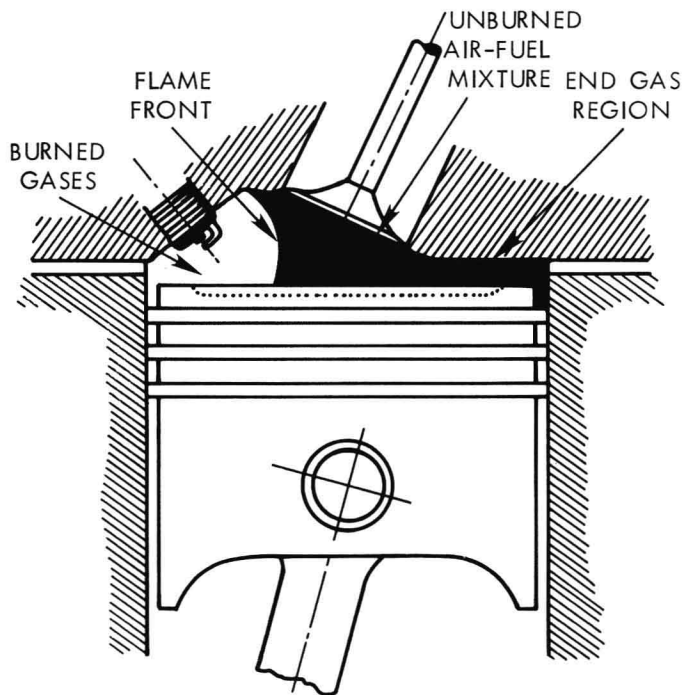


Figure 2. A diagram of the combustion chamber. The reader should note the "end gas region", an area which has been suggested to yield "bad" combustion chamber deposits.

Nevertheless, before a systematic improvement of the situation can be achieved, one must understand what the deposits are, in particular what they are made of and how they respond to various perturbations. In this book, we shall seek to determine the chemical nature of deposits formed within internal combustion engines. Before proceeding to the areas of current interest, we review some of the past work in the field. Because the nature of the deposits is dependent on the presence, or absence, of lead additives in the fuel, the review is divided into three parts, covering the period to 1930 (no lead additives), to the early 1970's (lead additives), and the most recent work on deposits formed from gasoline without lead additives.

## II. EARLY WORK IN DEPOSITS

One of the earliest discussions of deposits is that by Parish in an article on lube oils for World War I aircraft.<sup>1</sup> In the final figure of the article, one finds an illustration of the different forms of deposit found in different parts of the engine, with cylinder heads giving "soft and sooty" deposits and pistons giving generally "hard" deposits. Developing specifications for Liberty Aero Oil, Parish concluded that there was a correlation between Conradson carbon of the oil (residue following distillation) and carbon left in the engine. The final specification was that suitable oil would not show a Conradson carbon residue greater than 1.5%.

Orelup and Lee studied the factors influencing carbon formation in automobile engines.<sup>2</sup> As seen in the following, they correctly recognized the relationship between carbon deposits and knocking:

Carbon in an engine is like scale in a boiler. It is one of the best heat insulators. The temperature of fuel burning in a heat insulated cylinder soon rises above its critical temperature and thereupon breaks down in an extraordinary manner. This is manifested by knocking or detonating. Sudden large pressures are produced. To avoid the knocking, the operator must run with the spark retarded, thus losing power. There is an increased fuel consumption and a tendency for the engine to overheat. The car is no longer able to climb steep hills in high gear and in general lacks that desirable activity described as "pep".

Orelup and Lee recognized that engine deposits were not like graphite in character, more closely resembling "highly

condensed hydrocarbons of a bituminous nature". They further delineated the nature of the deposits:

The larger portion of the deposit consists of heavy hydrocarbons, some of them of a coke-like nature, possibly having a structure of interlinked carbon rings, and about 15% of a lighter hydrocarbon similar to lubricating oil. The mineral matter varies from 6 to 25%, according to the conditions of formation.... The organic portion contains small amounts of nitrogen and sulfur. Very few organic or inorganic solvents have any effect on cylinder carbon. A few of the most effective dissolve only a small amount of the lighter hydrocarbon. The best solvents found are monochlorobenzene, xylene, and cymidine, and to a lesser degree pyridine. Carbon deposits have the property in common with ordinary asphalts of forming a dark, soluble product with aqueous caustic soda, indicating material of an acidic nature resembling salts of weak bases.

They concluded that the key factor in creating deposits in automobile engines was the amount of lubricating oil projected into the combustion chamber. Although cars today consume far less oil than in 1925, it is still true that lubricating oil does contribute to deposit formation. However, one notes that the typical engines in 1925 consumed one quart of oil for every 150 miles, corresponding to the consumption of one quart of oil for every ten gallons of gasoline (at the 1925 mileage figure of 15 miles per gallon).

Certainly, in this time period, lubricating oil was considered responsible for deposit formation. W. A. Gruse performed more extensive studies implicating it in deposit formation.<sup>3</sup> Noting that oil-derived deposits formed in the crankcase, on the cylinder walls, and in the combustion chamber, Gruse proposed different mechanisms for the formation of each.

- crankcase - slow oxidation to form resins and asphaltenes.
- cylinder walls - low temperature coking in the piston ring grooves.
- combustion chamber volume - thermal decomposition of the lube, with little chance of oxidation, because the fuel consumes the oxygen present in the combustion volume.

However, with the introduction of lead into gasoline,<sup>4,5</sup> the relative contributions of fuel and lube to the deposit began to change, with the fuel becoming more important.

### III. ENGINE DEPOSITS CONTAINING LEAD

L. F. Dumont reported that the introduction of 1.5 ml tetraethyl lead per gallon fuel caused a fourfold increase in deposit weight over that for an unleaded fuel.<sup>6</sup> Doubling the tetraethyl lead content to 3.0 ml/gal. had only negligible effect on the deposit weight, suggesting that deposit attrition mechanisms might be operative. This possibility was confirmed by analysis of deposit accumulation through microscopy and x-ray diffraction which showed deposit growth to occur in three phases:

1. Accumulation of essentially carbonaceous material.
2. Accumulation of lead salts.
3. Attainment of equilibrium deposit quantity.

The distribution of lead salts was heterogeneous, with volatile, low melting point materials near the engine metal wall and with nonvolatile, high melting point materials at the deposit surface. Such a heterogeneity can create a thermal gradient with correlative thermal stresses, ultimately leading to deposit flaking.

Dumont postulated three possible mechanisms by which combustion-chamber deposits could increase octane requirement:

1. By occupying volume, the deposits increase the compression ratio of an engine and thus increase octane requirement. Dumont estimated the volume-effect to account for 10 to 47% of the total deposit knocking harm, with leaded fuel deposit volume contributing twice as much to ORI as the volume of unleaded fuel deposits.
2. By possessing an active surface, the deposits might "catalyze" various knocking reactions. No positive evidence for this effect was found.
3. By being a thermal insulator, the engine deposit could cause substantial increase in end gas temperatures, and therefore octane requirement by a) heating the charge drawn into the cylinder and b) by reducing the rate of heat dissipation from the hot compressed working fluid during compression of the end gas by the piston and by the advancing flame front. Dumont considered the thermal insulation effect to be the most important.

To actually experimentally separate the volume effect from

the thermal insulation effect, Dumont coated the inside surfaces of a single cylinder engine with a dispersion of Teflon in water, followed by a 750°F fusion. The octane requirement increased in direct proportion to the thickness of the Teflon film, with 25% of the ORI due to the volume effect, 75% of the ORI due to the insulating effect.

Consistent with previous work, Dumont believed that the carbonaceous portion of the deposit depended on the type of crankcase oil used and on the amount of oil reaching the combustion-chamber surfaces. This lube dependence was further confirmed in a comparison of ORI results between synthetic lubes (as a polyether and a polybutene, which gave low values of ORI) and conventional lubes (as neavy white oil and Coastal B which gave high values of ORI).<sup>7</sup>

However, this lube dominance of the carbonaceous portion of the deposit came into question as radiotracer experiments were used in engine research. The first radiotracer experiment performed on an engine deposit involved <sup>210</sup>Pb, and was used to demonstrate that new deposits will form at a more rapid rate on thick deposit surfaces than on thin surfaces or bare metal walls. Later, P. C. White reported <sup>14</sup>C results using either labeled benzene or toluene as a fuel and a synthetic polyglycol as a lubricant.<sup>9</sup> In the case of the benzene, deposits from the cylinder head showed 94% of the activity of the fuel and deposits from the piston in crowns showed 70% of the activity of the fuel, demonstrating that the fuel, not the lube, created the majority of the carbonaceous deposit. Similar results were obtained for toluene.

L.B. Shore and K. F. Ockert performed <sup>14</sup>C studies on labeled fuel with an L-head CFR engine employing a high quality 10W-30 motor oil.<sup>10,11</sup> They found that nearly all of the combustion chamber deposit came from the fuel; additionally, they noted:

1. The deposit-forming tendency of hydrocarbons goes up strongly with boiling point.
2. At a given boiling point, aromatics are more harmful than paraffins, while the olefins appear to be intermediate.
3. Boiling point is not merely an important factor in determining the deposit-forming tendency of aromatics; it seems to be the only factor. That is, as long as a compound contains at least one aromatic ring, its deposit-forming tendency can be predicted from its boiling point alone.

4. In an aromatic, all carbons in the molecule are equivalent with regard to their tendency to make deposits. That is to say, the carbon in the methyl group of toluene is as likely to end up in the deposits as the aromatic carbons.
5. On any given surface, the ratio of  $^{14}\text{C}$  labeled material to unlabeled material does not change systematically as the deposits build up.
6. There is, however, an effect of deposit location on concentration ratio, arising from variations of surface temperature within the engine.

Observation 4 of the above led Shore and Ockert to propose that engine deposits are formed via a pyrolysis of liquid-phase material. This hypothesis was considered to explain the difference in deposit-forming tendencies of aromatics and paraffins, for aromatics are more likely to "carbonize" than are paraffins. Nevertheless, Shore and Ockert were not able to reconcile observation 6 with this liquid-phase mechanism. The highest radioactivity concentration ratio occurred on the piston top (which showed the highest average temperature but the lowest total carbon). Although one might be tempted to propose that contributions from the lube "diluted" the intake valve deposits, Shore and Ockert considered this unlikely.

The single experiment arguing against significant lube contribution was performed in the CFR engine using benzene and labeled benzene as the fuel. The average concentration ratio of the deposit was 0.92, suggesting that the lube could contribute 0.08g/g, deposit. Shore and Ockert stressed that this result might not carry over to automotive engines under typical operating conditions. In fact, Sechrist and Hammen<sup>12</sup> reported a  $^{14}\text{C}$  radiotracer study involving labeled benzene in benzene with an uncompounded SAE 30 petroleum oil lubricant (standard CFR overhead-valve cylinder and piston) which showed the lube to contribute 0.5g/g, deposit. The message here is most likely that different lubes can contribute differently to deposit weight, with the key contributors to the deposit being the higher molecular weight, less volatile, components of both fuel and lube.

Other mechanisms interrelating engine deposits and octane requirement increase were proposed in the 1950's. Moxey<sup>16</sup> discussed the possibility of autoignition, the setting off of any flame front other than that initiated by the normal ignition, which would result in more rapid compression of the end gas, and thus more knock. Mikita and Bottoney<sup>14</sup> divided this concept into preignition (ignition before the spark is passed,



equivalent to advancing the spark) and postignition (ignition of some of the charge after the spark is passed). By injecting engine deposits into the combustion chamber of a six-cylinder engine, they were able to induce preignition. Such an effect could have a dramatic effect on ORI, for inflammation of a charge  $10^\circ$  before spark passage can increase octane requirement 5 to 10 units. Mikita and Bottoney noted that in some cases preignition, or postignition, occurred to such an extent that the engine continued to operate with the ignition turned off, a phenomenon they called run-on.<sup>14</sup> In addition to the previously proposed thermal insulation effect, Mikita and Sturgis<sup>15</sup> suggested that the finite heat capacity of the deposits would also adversely affect octane requirement by heating the incoming charge.

Very little of the early work on deposits dealt with chemistry. The statements of Orelup and Lee<sup>2</sup> were prescient, and White<sup>9</sup> presented carbon, hydrogen, and oxygen analyses for unleaded fuels. At the end of the 1950's, Lauer and Friel<sup>17</sup> presented work which not only contained detailed chemical analyses but also advocated the theory of deposit formation from the gas phase, rather than from the previously assumed liquid phase.

Lauer and Friel conducted their experiments on a single cylinder, L-head Lauson engine, initially using a leaded commercial fuel and a multigrade lubricating oil. Consistent with the work of Dumont,<sup>6</sup> they noted carbonaceous deposits to accumulate first, followed by increasing amounts of lead compounds after 15 hours. The deposits had H/C ratios ranging from 0.72 (valve area) to 0.84 (piston top). To focus on the carbonaceous portion of the deposit, they used two fuel/lube combinations with no metallic species: iso-octane fuel (=2,2,4 trimethylpentane) with hydrocarbon lubes [to study lube contributions to the deposit] and toluene fuel with synthetic (polyether) lubes [to study fuel contribution to the deposit]. To facilitate examination of the deposits, removable plugs were inserted into the combustion chamber head, thereby allowing both deposit thickness measurements and electron microscopic analysis.

The combination of toluene fuel with a paraffinic lube gave the deposit of most weight (1.2g) and lowest density (0.23 g/mL). The iso-octane/naphthenic lube combination gave less weight (0.4g) but a high density (0.65 g/mL), thus suggesting that different hydrocarbon combinations did yield different deposits. However, electron microscope studies suggested all deposits to be similar, consisting of agglomerates of small spheres of varying density and packing. Noting that carbon

formed in the gas phase from diffusion flames was also spherical, Lauer and Friel suggested the deposits to be gas phase in origin.<sup>17</sup>

These deposits were analyzed in terms of chemical composition, Soxhlet extractability, and infrared spectroscopy. They contained between 20 and 36% by weight oxygen, with H/C ratios ranging from 0.55 to 0.91. The highest extractability was for the iso-octane/naphthene combination in pyridine (40%). Two features in the infrared spectrum were associated with oxygen functionality: a peak at  $1724\text{ cm}^{-1}$  (saturated monobasic carboxylic acids, and possibly aldehydes, ketones, esters, or anhydrides) and at  $1587\text{ cm}^{-1}$  (ionized salts of carboxylic acids). Consistent with the interpretation of the infrared in terms of acids, Lauer and Friel noted that decarboxylation seemed to account for most of the weight loss on heating to ca.  $610^{\circ}\text{C}$ . Furthermore, Lauer and Friel generated "simulated engine deposits" of comparable oxygen content by torching lube oil which had been placed on a rotating metallic disk.

In terms of previous theories interrelating ORI and deposit characteristics, Lauer and Friel pointed out that observed ORI was inversely dependent on the bulk density of the deposit, a result consistent with both the volume and thermal insulation effects proposed by Dumont.

In addition to affecting the octane requirement of an engine, combustion deposits can influence the chemistry of exhaust gases leaving the engine. With increased concern about pollutants as  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ , and unburned hydrocarbons, a number of studies were made on the relationship between deposits and gas phase emissions.<sup>18-22</sup> Both wall temperature and surface roughness affect hydrocarbon emissions, with lower temperatures and rougher surfaces enhancing hydrocarbons in the exhaust.<sup>23</sup>

This concern about gas phase pollutants has caused a return to unleaded fuels. The catalytic converters of most new cars, which are designed to lower amounts of  $\text{CO}$  and unburned hydrocarbons, are poisoned by lead fuel. Thus, the combustion chamber deposits formed within these new cars are composed primarily of carbon, just as they were in 1925, when Orelup and Lee wrote their classic paper!

#### IV. RECENT WORK ON DEPOSITS FROM UNLEADED FUELS

With the return to unleaded fuel in the 1970's, the deleterious effect of deposits on octane requirement again became an

issue. It is difficult, from both an economic and energy conservation standpoint, to produce high octane unleaded fuel, with the size and composition of the clear octane pool allowing a 91 RON unleaded gasoline.<sup>24</sup> With this lower octane rating, and correlative diminished compression ration of new automobiles, the octane requirement increase problem is again with us. Should the final octane requirement of a new car exceed the octane of available unleaded fuel, engine knock is inevitable.

Benson has reported octane requirement increases for General Motors cars equipped with emission control hardware and low compression engines designed to run on unleaded fuel.<sup>25</sup> He found that greater octane requirement increases occurred with:

1. An engine oil containing bright stock compared to an engine oil without bright stock. (bright stock is a high molecular weight, aromatic-containing, material derived from deasphalted vacuum residuum).
2. An unleaded fuel which contains a polymeric detergent-dispersant additive relative to conventional additive packages.
3. Customer-type driving relative to rapid mileage accumulation on a dynamometer.

With respect to the relationship of ORI to engine deposits, Benson stated that all of the ORI with unleaded fuel could be eliminated by removing combustion chamber deposits, with about two-thirds of the ORI specifically caused by deposit accumulated in the end-gas region of the chamber.<sup>25</sup> With reference to the mechanisms of Dumont,<sup>6</sup> Benson stated that ten percent of the ORI is due to the volume effect, the other 90 percent probably due to the thermal effect.<sup>25</sup> Benson noted that octane requirement increase was not affected by the lead content of the fuel.

In a study of the effect of lubricant viscosity index improvers on ORI, Bachman and Prestridge discussed physical and chemical characteristics of deposits formed within a 1975 model car (350 cid OHV V-8) using commercial unleaded fuel.<sup>26</sup> Electron microscopy indicated the carbon to be amorphous (non-graphitic), extremely porous, and characterized by a heterogeneous granular structure. They noted that the observed morphology was consistent with a pyrolytic mechanism, and thus distinct from the spherical deposits reported by Lauer and Friel.<sup>17</sup> Heat capacity values were found to be 0.40 and 0.44 cal/(g°C), and the density was  $1.53 \pm 0.02$  g/cc. Microanalysis of deposits showed about 63 wt% carbon, 5 wt% hydrogen and 2 wt%