

THE CITY UNIVERSITY
THERMO-FLUIDS ENGINEERING RESEARCH CENTRE

ABSTRACT

This report describes a series of tests carried out during October 1987 - January 1988 using a proposed additive for combining water and diesel type fuels, with a view to establishing the risks, or otherwise, of corrosion problems developing and of the fuel-water-additive mix breaking down.

It is concluded that stable solutions of water and diesel fuel can be created which are reasonably compatible with several of the materials likely to be encountered in diesel fuel systems. Materials tested included steel, aluminium, copper, brass, Bundy tubing, rubber, and reinforced nylon.

STABILITY AND MATERIALS COMPATIBILITY
TESTS OF A PROPOSED DIESEL
FUEL ADDITIVE

by

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1. INTRODUCTION

Numerous past attempts to combine small amounts of water with diesel, either mechanically or chemically, have shown limited success. The emulsions created have been unstable, separating out within minutes. There have also been significant corrosion problems associated with the use of such emulsions in diesel systems, often leading to research programmes being abandoned.

However, recent research has led to the development of a diesel additive which overcomes the major hurdle of instability. The use of this additive has enabled over 10% of water to be completely absorbed in diesel. The additive, which is a combination of various organic compounds, has been successfully employed to create not only a diesel—water emulsion but also a clear stable solution.

Obviously a large amount of testing is required in order to support this new innovation and so a comprehensive test program has begun at The City University, London.

Initial tests have been conducted using:

- i) The additive (ADD1—10/1)
- ii) A clear solution of diesel, water and additive in the ratio 30 : 3 : 4.
- iii) An emulsion of diesel, water and additive in the ratio 30 3 : 2.

The solution and emulsion detailed above were labelled S1 and E2 respectively.

This report outlines the experiments performed to date to investigate the stability and materials compatibility of the mixtures and discusses the results obtained.

2. TEST PROGRAM

In order to establish the merits of the new fuel additive under investigation (subsequently referred to as ADD1-10/1), and also to discover any problem areas that may arise from its use, a number of bench tests were performed. These tests are detailed below.

2.1. Static Corrosion Test

The basic diesel fuel system was divided into its components:

TANK - FUEL LINE - FILTERS - PUMP - INJECTORS

From contact with various diesel plant manufacturers and suppliers, the component materials typically used were ascertained to be:

Metallic	Non—Metallic
Structural steel	Reinforced nylon tubing
Cold—drawn steel tube	Bundy tube
Aluminium alloy	Rubber
Brass	
Copper	

These materials were corrosion tested at room temperature (20°C). Two control tests were set up for each sample:—

- i) Air — in order to compare test samples with an original sample.
- ii) Diesel — in order to recognise any 'normal' effects due to contact with untreated diesel.

The test fluids used for each material sample were initially:—

- i) Solution S1 — consisting of 30 ml diesel + 3 ml water + 4 ml ADD1—10/1.
- ii) Solution E2 — consisting of 30 ml diesel + 3 ml water + 2 ml ADD1-10/1.

Later further corrosion tests were conducted using solution S1 mixed with various proprietary diesel fuel improvers.

Each material sample was carefully cleaned (using emery cloth on the metallic and tissue on the non—metallic samples) and then fully immersed in the test fluids.

Using tongs, each sample was then individually removed from its jar of fluid, dried using tissue and weighed on Mettler AE16O electronic scales (range 0 — 160 mg, readability 0.1 mg). The weight was recorded and the sample returned to its jar of fluid.

The samples were left undisturbed for two months during which time any visible changes in samples or fluids were recorded (see Plate 1). After two months, the samples were re-weighed using the same technique as before to establish whether any weight gain/loss has occurred.

2.2. Tank Corrosion Test

Since tank corrosion is usually initiated at the interface between the liquid and the air above, a test was set up to simulate conditions in a fuel tank.

Narrow strips of mild steel were placed in bottles half-filled with test fluids solution S1 and emulsion E2 and control fluids diesel and water (as shown in Plate 2). One set of these four bottles was left undisturbed, another was inverted once and then left undisturbed and a third set was inverted daily. The tops of the bottles were loosened to allow air into the bottles and the effects of corrosion were observed.

2.3. Emulsion Separation Test

In order to establish whether it would be feasible to use the additive ADD1—10/1 with diesel and water in an emulsion form, a test was set up to observe the stability of such an emulsion and the effects that certain materials had on it.

Samples of the reinforced nylon tube, rubber, and brass were placed at the bottom of three 25 ml measuring cylinders. Emulsion E2 was then poured onto the samples up to the 25 ml mark and also into a fourth measuring cylinder to act as the control. The separation of the emulsion was recorded periodically.

2.4. Comparison of ADD1—10/1 with proprietary 'water absorbent' diesel fuel additives

Some diesel improvers are currently being marketed advertising an ability to absorb moisture in the system. A short comparison test was set up between ADD1—10/1 and these other diesel improvers by adding 10% water to the additives and vigorously shaking the samples to distribute the water. The specimens were then left to stand.

2.5. Effect of % Addition of ADD1—10/1 on a fixed diesel/water ratio

This examination was performed in order to establish how critical the relevant amount of ADD1—10/1 was in obtaining a usable water-containing diesel fuel mixture. For this test, 3 ml of water was mixed with 30 ml of diesel. 1, 2, 3,6 ml of ADD1—10/1 was then added to this mixture and the results noted.

2.6. Diesel Contamination Tests on Solution S1

Since the solution S1 is designed to be used in standard diesel systems, the effects of the further addition of diesel on it were investigated. The following proportions of diesel and solution S1 were mixed together and the immediate reaction recorded:—

Diesel	%Solution S1
95	5
90	10
85	15
80	20
70	30
60	40
50	50
30	70
10	90

After these mixtures had been left undisturbed for 3 weeks, a second observation was made.

2.7. Acidity Tests

Acidity tests were carried out on various combinations of diesel, water and ADD1-10/1 using a Kent Industrial Measurements Ltd. Model 7020 laboratory pH meter.

After initially stabilizing the meter, the probes were immersed in approximately 70 ml of ADD1—10/1 and the liquid was agitated using a glass rod. An initial reading was taken and the liquid was then left for 10 minutes after which a second reading was taken. Two further readings were taken by switching the meter to 'check' and back to 'auto' in order to examine the stability of the readings. An average pH value could then be obtained (neglecting the initial reading).

Further acidity tests were later performed on modified versions of the additive ADD1—10/1. These modified additives were labelled ADD2—10/1, ADD3—10/1, ADD4-10/1, and ADD5—10/1.

3. RESULTS

3.1. Static Corrosion Test

The visual results may be summarised as follows:—

TEST MATERIAL	REACTION
Structural steel	No visible change had occurred to any of the fluids. The samples from the diesel, solution S1 and emulsion E2 were all slightly tinted brown.
Cold—drawn steel tube	No visible change had occurred to either the test sample or any of the fluids
Dural aluminium alloy	No visible change had occurred to any of the test fluids. The samples from the solution S1 and emulsion E2 both had a slight gold tint.
Brass	Each of the fluids containing the ADD1—10/1 had shown a reaction. The emulsion E2 had been discoloured (grey) and the solution S1 was discoloured with a dark black haze at the bottom of the jar. In ADD1—10/1 green wisps had appeared in the fluid around the top of the brass. In all samples containing ADD1—10/1, the brass had been blackened.
Copper	A reaction had occurred in all samples containing ADD1—10/1. The emulsion E2 had been clearly discoloured (blue) and solution S1 had separated into three visible layers. The ADD1—10/1 had been discoloured (pale green). In each of the samples containing diesel and ADD1—10/1 the copper had been darkened. ADD1—10/1 alone had etched the surface of the copper leaving it a dull pink colour.
Reinforced nylon tubing	The nylon samples in the fluids containing water have turned slightly opaque. In the diesel sample and the ADD1-10/1 sample the nylon has changed to the colour of the liquid. The nylon tubing appeared to accelerate the separation of the emulsion E2.
Bundy tube	The bundy tube increased the rate of separation of the emulsion E2 slightly but other than this, no visible reaction had occurred.

Rubber Again, the rubber increased the rate of separation of emulsion E2. The rubber had also visibly expanded in solution S1 and emulsion E2.

Table 1. Static Corrosion Test (Visual)

The effects of the various fluids on the weight of each material sample are tabulated below. The figures show the percentage weight loss (—) or gain (+) of the sample from its original weight.

	Air	Diesel	Solution S1	Emulsion E2	ADD1—10/1
Structural steel	0	-0.01	-0.01	-0.01	-0.02
Cold—drawn steel tube	0	-0.01	0	-0.04	-0.03
Dural aluminium alloy	-0.01	0	-0.01	0	-0.01
Brass	0	-0.01	-0.08	-0.05	-0.02
Copper	0	-0.01	-0.20	-0.28	-0.14
Reinforced nylon tube	0	-0.37	-2.23	-1.37	+1.04
Rubber	+0.01	+63.66	+84.26	+83.22	+7.52
Bundy tube	-0.11	+3.59	+7.97	+8.37	+1.98

Table 2. Static Corrosion Test (Weight)

3.2. Tank Corrosion Test

The only liquid sample to show any sign of corroding the steel in any of the sets of bottles was water. Emulsion E2 and solution S1 both left the steel perfectly clean, as did the diesel.

3.3. Emulsion Separation Test

Plate 3 shows the emulsion samples at 4 weeks old. Although considerable separation

has already occurred, within a further 4 weeks, the emulsion samples containing the non—metals were to separate to the extent that no opaque layer was visible. The opaque layer in the sample containing brass and in the control was also greatly reduced over the 8 week period.

3.4. Comparison of ADD1-10/1 with other 'water absorbent' diesel fuel additives

When the water was added to the diesel additives a reaction was seen to occur in the ADD1—10/1 sample immediately. The other diesel fuel improvers, although appearing slightly cloudy when vigorously shaken, very quickly separated into two layers. The ADD1—10/1 sample remained a homogeneous clear pale yellow liquid even after standing. A piece of mild steel was inserted into each sample. Although this gave no reaction with the ADD1—10/1, considerable corrosion occurred in the steel in the other additive samples.

3.5. Effect of % Addition of ADD1—10/1 on a fixed diesel/water ratio

The following results were recorded:-

1 ml ADD1-10/1	In this sample a white substance resembling white gloss paint formed which settled to the bottom of the jar. The bulk of the liquid was a semi—clear red.
2 ml ADD1-10/1	This created an emulsion with an appearance similar to creme shampoo. This emulsion appeared relatively stable. After 3 weeks it had, however, separated into four layers.
3 ml ADD1-10/1	This created a reddish solution with a blue haze to it. Even after 3 weeks this solution remained stable with no visible separation occurring.
4 ml ADD1-10/1	A clear diesel—red solution was obtained with no haze and no separation of fluid occurring.
5 ml ADD1-10/1 6 ml ADD1-10/1	No further improvement could be made to the solution containing 4 ml ADD1-10/1. A similar clear diesel—red solution was obtained using these quantities of ADD1-10/1 although these solutions turned very slightly cloudy after standing for 3 weeks.

3.6. Diesel Contamination Tests on Solution S1

% Diesel	% S1	INITIAL REACTION	RESULTS AFTER STANDING FOR 3 WEEKS
95	5	Large white flakes formed which slowly settled on the bottom	Two layers visible: top layer — clear diesel—red; bottom layer — pale yellowy pink waxy layer (~1 mm thick).
90	10	Slightly smaller white flakes formed, settling to the bottom	Separation similar to that obtained with 5% S1 except the waxy layer appears to be a little thicker (~2 mm thick).
85	15	Small white flakes drifted to bottom of the jar	White deposit at bottom of jar did not cover the entire bottom of the jar. Clear diesel—red solution above.
80	20	Small opaque particles formed, slowly settling to bottom of jar	Fine particles collected on base of jar (less than for 15% S1).
70	30	Very small opaque white particles formed	No deposit visible but liquid has separated into 2 layers. Top layer — clear diesel—red bottom layer — clear yellowy orange.
60	40	An emulsion formed	Separation into 2 layers: clear diesel—red layer on top and cloudier layer below.
50	50	Emulsion formed similar to creme shampoo	Separation into 2 layers: clear red on top, cloudy pink below.
30	70	Hazy liquid formed	Homogeneous hazy liquid.

10	90	Virtually clear liquid formed	Homogeneous liquid with slight bloom.
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Table 3. Diesel Contamination Test

3.7. Acidity Tests

The initial acidity tests gave the following results:

SAMPLE	AVERAGE pH VALUE	MAXIMUM DEVIATION
ADD1—10/1	10.22	0.04
Solution S1	10.14	0.04
Emulsion E2	10.08	0.04
Diesel + ADD1—10/1	9.55	0.03

Table 4: Acidity Test 1.

Subsequent tests on the modified versions of the additive ADD1-10/1 produced the following results.

SAMPLE	TEST 1		TEST 2		TEST 3	
	AVERAGE pH VALUE	MAX. DEVIAT.	AVERAGE pH VALUE	MAX. DEVIAT.	AVERAGE pH VALUE	MAX DEVIAT.
ADD1—10/1	9.61	0.02	9.58	0.01	9.53	0.02
ADD2—10/1	9.66	0.03	9.83	0.02	9.68	0.03
ADD3—10/1	9.49	0.01	9.86	0.02	9.60	0.02
ADD4—10/1	9.58	0.01	9.82	0.01	9.75	0.03
ADD5—10/1	9.66	0.03	9.88	0.02	9.79	0.04

Table 5. Acidity Test 2

Tests were also attempted on diesel—water solutions containing these additives but the readings obtained were very unstable.

4. DISCUSSION

The static corrosion test results showed that separation occurred to some extent in all the samples of emulsion E2. However, in the cases of the steels and aluminium alloy it was thought that the metal had no effect on this separation.

Of the eight materials tested, the only metallic ones to show a visible reaction were the copper and brass. It will be necessary to establish whether this reaction is purely an initial reaction providing a surface coating on the sample or whether it is a progressive reaction, continuing to attack the metal. It is also necessary to ascertain whether the fluid itself is being decomposed.

None of the non—metals appears to dramatically affect the liquids although the rubber sample did darken the ADD1-10/1. The rubber and the reinforced nylon tube gave more obvious reactions than the Bundy tube and these results together with the copper and brass samples are shown in Plate 1.

The most prominent feature in Table 2 (showing weight losses and gains of the samples) is the dramatic increase in weight of the rubber samples. This large gain is due to the rubber absorbing liquid which affects its strength and flexibility. Although the weight increases were very large for the samples in solution S1 and emulsion E2, the diesel control sample showed a similar massive increase so this type of rubber would obviously not be used reliably in diesel systems. A more significant result may be that shown with the Bundy tube where the weight increase in the samples exposed to solution S1 and emulsion E2 is greater than twice that experienced with diesel.

It should be noted, when considering the results for all the non—metals (and also the aluminium alloy), that since the initial weights of these samples were comparatively small, the experimental error is significant. This error is due to the drying process that the specimens underwent prior to being weighed. Although extreme care was taken to dry the samples thoroughly and uniformly without removing any surface layer from them, the method was clearly open to error. This factor is highlighted by the apparent weight loss of the aluminium sample used in the air control. Careless drying of the reinforced nylon tube sample in ADD1-10/1 could also account for some of its recorded gain in weight.

Another potentially misleading factor in this experiment was the variation in shape and size of the different material samples. Since the brass samples were cylindrical, the cold—drawn steel roughly cuboid, and the other metallic samples flat, the surface area/volume ratio of the brass was significantly smaller than that of, say, the structural steel or copper. Therefore any reaction affecting the surface of the sample would appear less significant in the brass samples

than with the other metals.

Accounting for these possible sources of error, the only metallic samples to show unmistakable changes in weight were the copper and brass. Both suffered weight losses when exposed to solution S1 and emulsion E2. The most probable cause of this weight loss would be that either the surface was being etched away by the liquid or that the surface coating was removed from the metal during the drying procedure or possibly a combination of these two factors. Further tests may clarify the reason for the loss in weight.

The results from the tank corrosion test illustrate that the use of ADD1—10/1 in diesel—water mixtures enables the water to be completely absorbed since there is no visible reaction with the steel. Although this test indicates that either solution S1 or emulsion E2 could be used in diesel fuel systems the emulsion separation test shows that the instability of the emulsion could create problems. The rate of separation of the emulsion is clearly affected by the material with which it is in contact although even the control sample showed considerable separation after 8 weeks.

The comparison test between ADD1—10/1 and other fuel additives clearly demonstrated that only ADD1-10/1 could absorb 10% of water. Further investigations showed that the other “water absorbent” additives failed to absorb even 0.5% water in diesel.

The percentage addition of ADD1—10/1 on a fixed diesel—water ratio required to provide a clear solution was found to be relatively flexible provided that an equal or greater quantity than that of water was added. However, a slight clouding in the resulting solution was experienced when excess amounts of ADD1—10/1 were added.

The diesel contamination test results indicate that some problems might arise if a diesel—water mixture containing ADD1-10/1 (for example, solution S1) is used in conjunction with untreated diesel. This situation could lead to blocking up of filters in the low pressure area of the fuel system, but any “sediment” passing through the filters may be forced through the injectors at high pressure. This could have an effect on the combustion of the fuel.

Finally, the acidity test results indicated that ADD1-10/1 and modified versions of this additive and also diesel mixtures containing ADD1—10/1 all show pH values between 9.5 and 10.5. This corresponds to slightly alkaline conditions. Although a certain amount of instability in the instrument reading was experienced when measuring pH values of any mixtures containing diesel, this instability became excessively large when measuring diesel-water mixtures containing modified versions of ADD1—10/1.

The effect of ageing of the additive samples (Table 5) has so far shown no particular trend although further tests are currently being conducted.

5. CONCLUSIONS AND FURTHER WORK

The project illustrated that by using additive ADD1-10/1, diesel and water could be successfully mixed to form either an emulsion or a clear solution. From the tests it may, however, be concluded that the emulsion would not be a suitable fuel if left to stand for any length of time because of the separation that occurs. Therefore future effort will be concentrated on the examination of the solutions.

The static corrosion tests produced encouraging results for the steels and aluminium alloy samples. Although some problems were encountered with the copper and brass samples, further tests have already begun with fresh samples of ADD1—10/1, and solution S1 in an investigation as to whether or not the reaction experienced by these samples is progressive. It is also hoped to further these bench tests by examining the effects of recirculating flow.

The acidity tests carried out indicated that the additive ADD1-10/1 was alkaline (pH 9.5 - 10.5). Another area for further work would be the possible neutralization of this additive or at least a reduction in its alkalinity. If this could be achieved, the extent to which it reacts with, for example, brass and copper may be reduced, which will obviously increase its range of application.